ICOSAHEDRAL

CARBORANE

DERIVATIVES

Mark Alexander Fox B.Sc.(Dunelm)
St. Hild and St. Bede

A thesis submitted to the University of Durham
in candidature for the Degree of Doctor of Philosophy

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To Mum and Dad.....

DECLARATION

The work described in this thesis was carried out in the University of Durham between October 1988 and September 1991. It has not been submitted, either completely or in part, for another degree in this or any other University and is the original work of the author except where acknowledged by reference.

ACKNOWLEDGEMENTS

I wish to thank Prof. K. Wade, Dr. J.A.H. MacBride and R. Coult for their helpful discussions. Financial assistance from S.E.R.C. and D.U.S.H.I.S. are gratefully acknowledged. I would also like to thank J. Milner for typing this thesis.

ABSTRACT

M. A. Fox B.Sc.

This thesis describes some new derivative chemistry of the icosahedral carboranes, 1,2- and 1,7-$C_2B_{10}H_{12}$, related to the incorporation of carborane polyhedra in Victrex-type polymers (polymers incorporating para-disubstituted benzene rings linked through ether and ketone functional units).

It begins with a survey of relevant carborane literature, and reviews the spectroscopic techniques by which carborane derivatives can be characterized. The syntheses of a range of boron-iodo carboranes by reaction of iodine, nitric acid and sulphuric acid with the parent carboranes are described, and the ^{11}B and ^{13}C n.m.r. spectra of the products are discussed.

Syntheses and model reactions of series of diarylcarboranes $R'R''C_2B_{10}H_{10}$ (in which the aryl substituents R′ and R′′ have functional groups suitable for their incorporation in polymers) are described, including the previously unknown 1,9- and 1,12-bis(4-carboxyphenyl)-*ortho*-carborane, 1,7-bis(phenoxyphenyl)-*meta*-carborane and 1,7-bis(4-carboxyphenyl-*meta*-carborane - 4,4′-diphenoxybiphenyl polymer. A new and efficient method of 1,7-diaryl-*meta*-carboranes from *meta*-carborane with butyllithium, copper (I) chloride and aryldiazonium tetrafluoroborate as reagents is described.

Several C-substituted hydroxy, mercapto and amino derivatives of *ortho*- and *meta*-carborane have been prepared and deprotonated using triethylamine of N,N,N′,N′-tetramethyl-1,8-diaminonaphthalene (proton sponge). The molecular structure of the proton sponge salt of 1-phenyl-2-mercapto-*ortho*-carborane, $[PhCB_{10}H_{10}CS]^-[C_{10}H_6(NMe_2)_2H]^+$, has been determined and found to contain cage distortions which are rationalized by frontier molecular orbital considerations. Structures of 1-phenyl-2-phenylethynyl-*ortho*-carborane, 1-phenyl-2-(4-methylphenyl)azo-*ortho*-carborane, 1-phenyl-2-(4-methoxyphenyl)-*ortho*-carborane and 2,2′-bis(1-phenyl-*ortho*-carboranyl) trisulphide, determined by X-ray crystallography, are reported.

CONTENTS

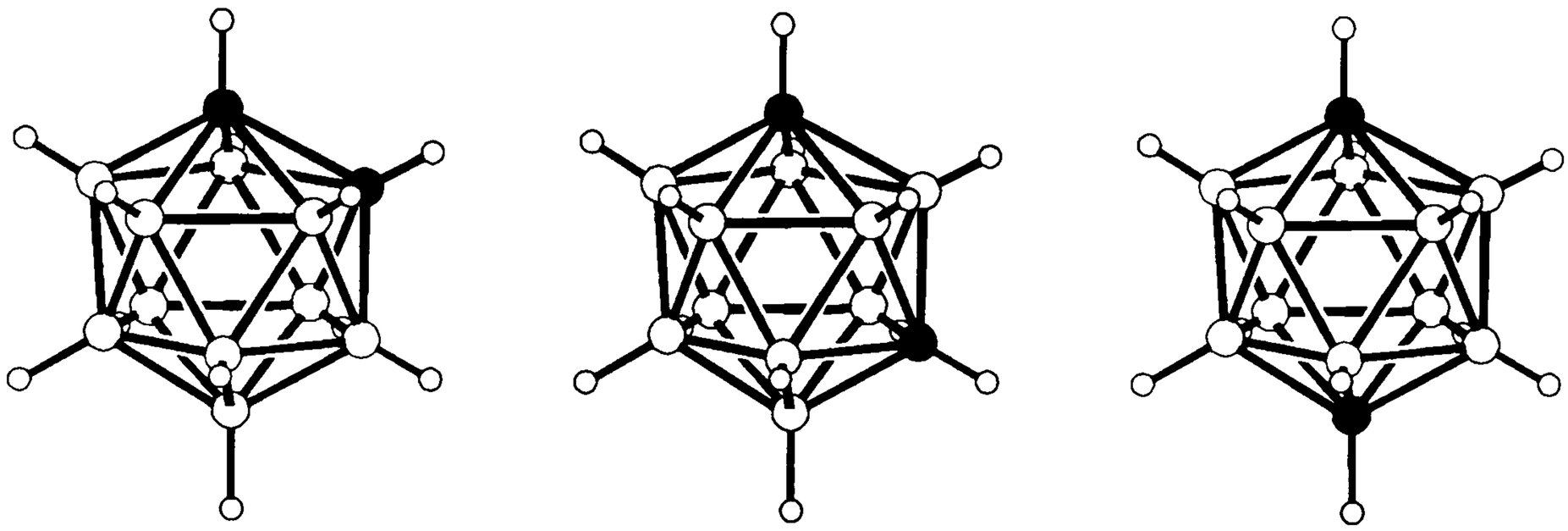
CHAPTER 1

INTRODUCTION

This chapter describes the carboranes, their potential applications and a summary of the aims of this study.

INTRODUCTION

Carboranes are mixed hydrides of carbon and boron in which the skeletal carbon and boron atoms are arranged on the vertices of a triangulated polyhedron. This study concerns the icosahedral carboranes of molecular formula, $C_2B_{10}H_{12}$, and their derivatives. There are three $C_2B_{10}H_{12}$ isomers, *ortho*, *meta* and *para* which are shown below. These isomers are chemically very robust and have extensive derivative chemistries[1].



ortho *meta* *para*

○ = B ● = C ○ = H

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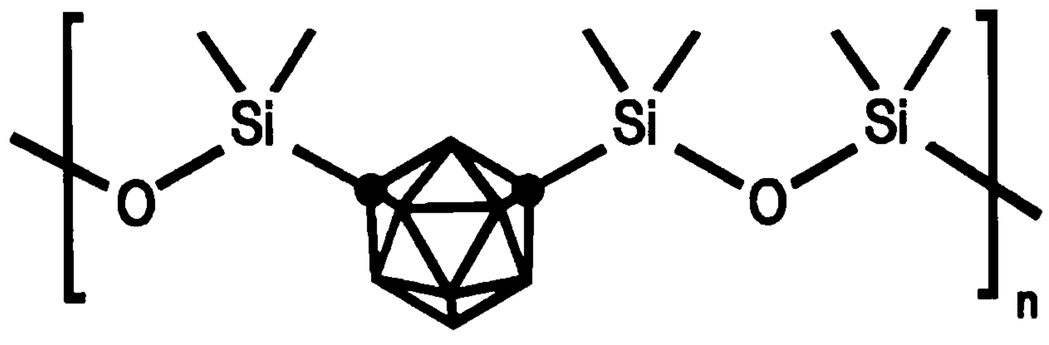
POTENTIAL APPLICATIONS OF ICOSAHEDRAL CARBORANES

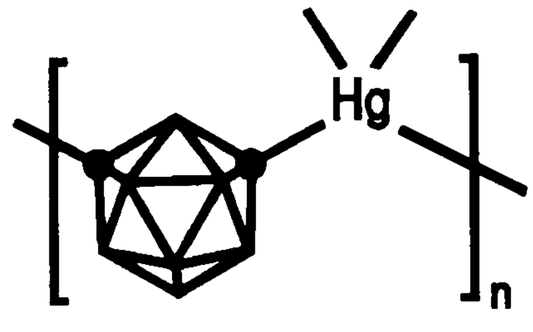
Icosahedral carboranes have good thermal stabilities so they have been used to synthesize polymers with excellent resistance to degradation by heat and air oxidation[1a,b]. The best known carborane polymers are marketed as 'Dexsils'. These are polycarboranylsiloxanes with outstanding thermal and chemical properties as the carborane cage acts as a stabilizer by its inductive effect on the silyl groups. These polymers can be used as high temperature gaskets, O-rings, electrical connector inserts, coatings, gas chromatography stationary phases, oils, greases, adhesives, rigid foams and fire retardants.



Dexsil 300

Other high temperature carborane polymers are shown below as examples.

Polymetallocarboranes e.g.[2]



 = *ortho* $-CB_{10}H_{10}C-$  = *meta* $-CB_{10}H_{10}C-$

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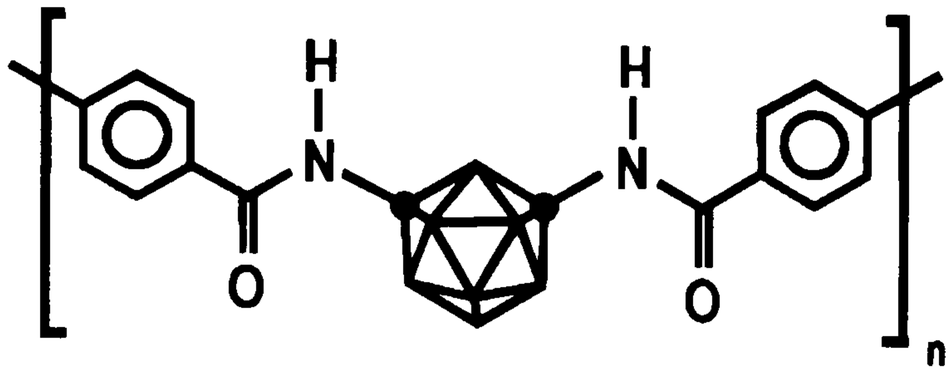
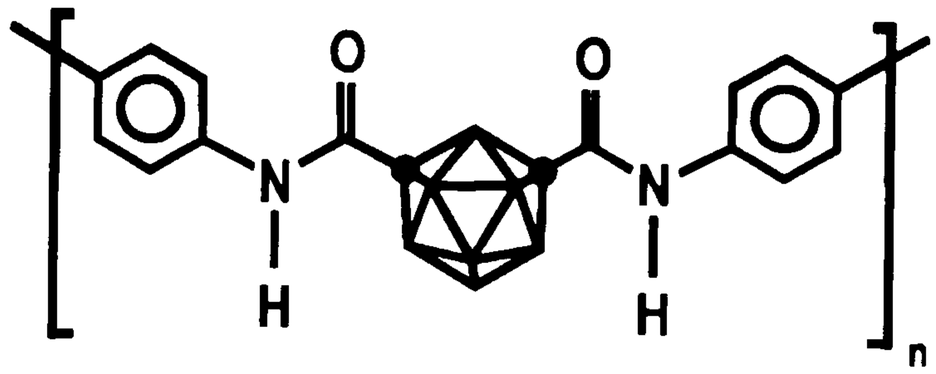
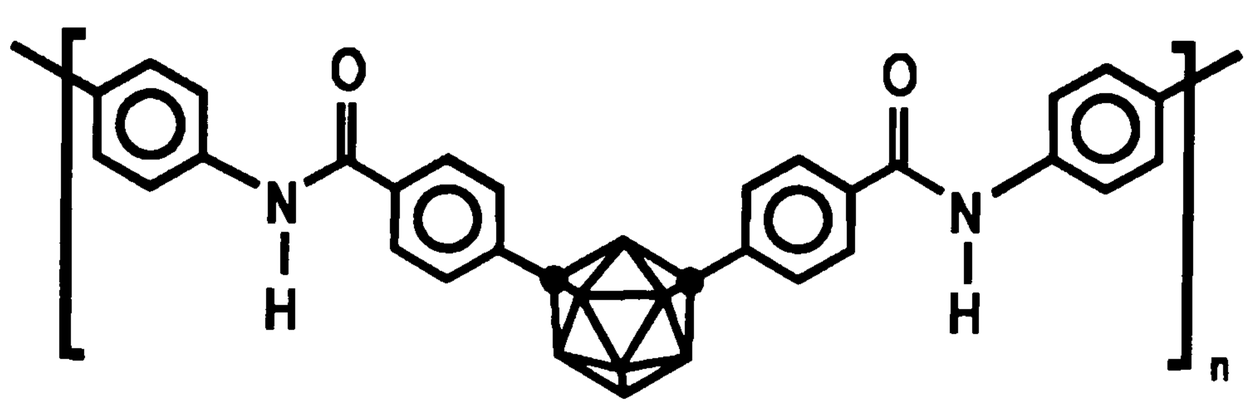
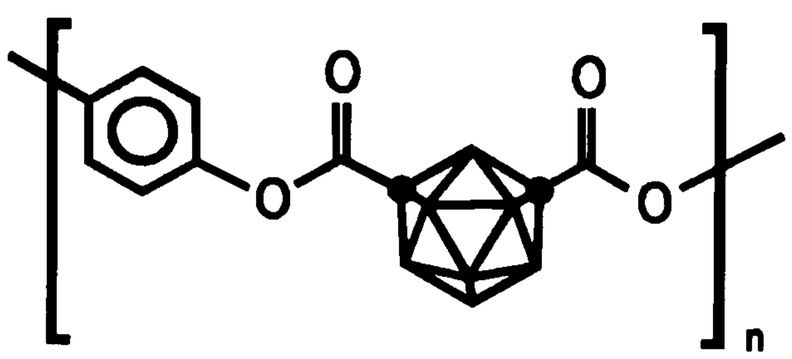
Polyamides e.g.[3,4,5]

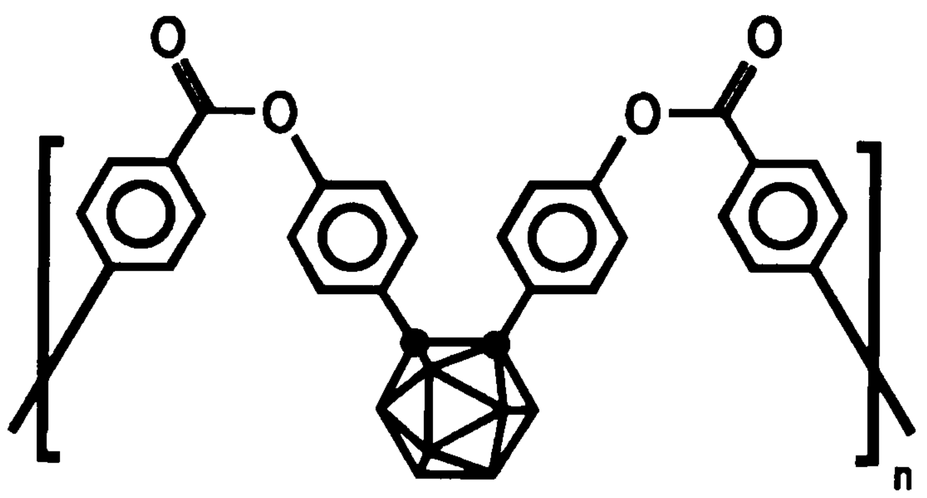


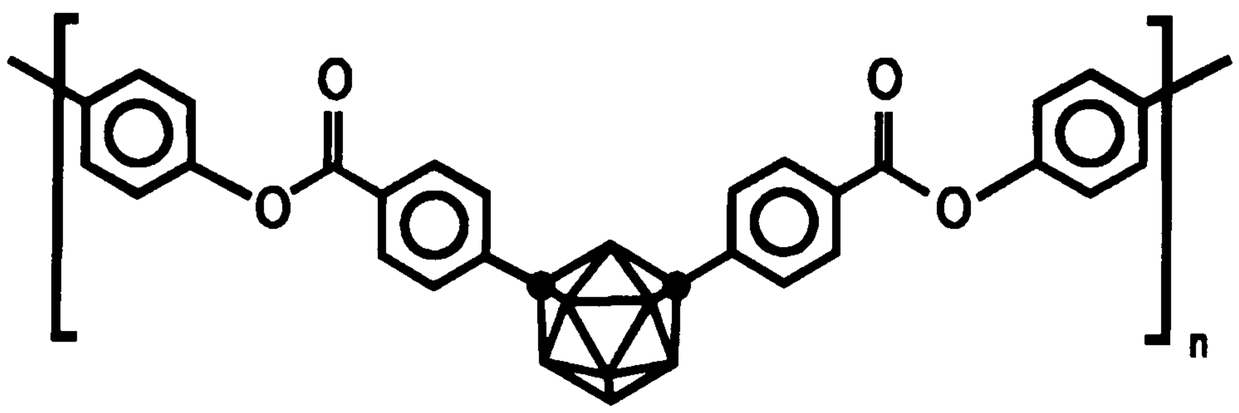




Polyesters e.g.[6,7,8]







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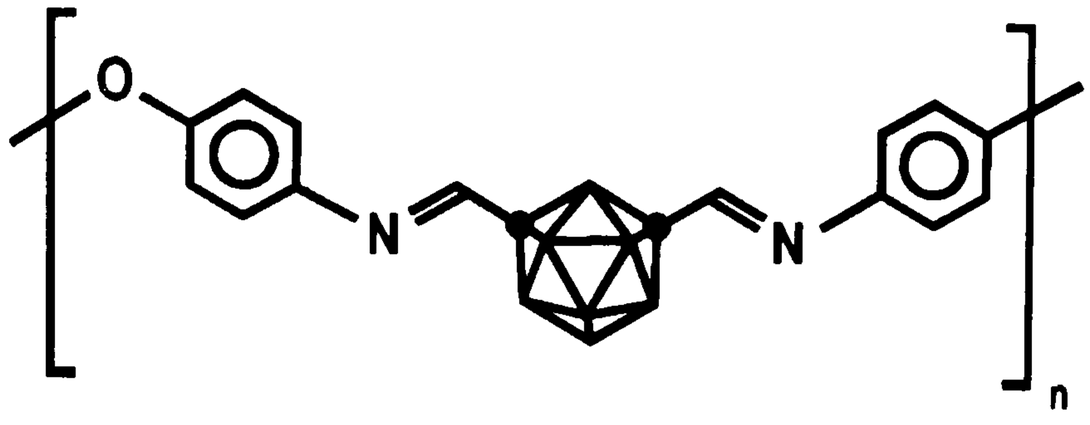
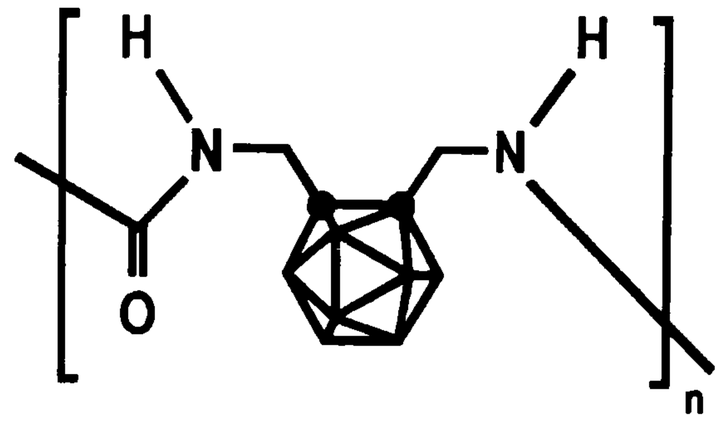
Polyazomethines e.g.[9]



Polyurethanes e.g.[10]



The major impact of the carborane moiety on the thermal properties of carborane polymers, with respect to non-carborane polymers, is seen in the behaviour of these polymers at temperatures above 450°C. For example aromatic polyesters degrade extensively with weight loss of 60% at 500°C whereas the carborane-containing analogues lose only 5-10% of their weight at 900°C[11]. Hydrogen elimination from B-H groups at temperatures above 500°C in carborane-containing polymers generates non-volatile residues with B-B crosslinks[12,13]. If the polymer contains aromatic rings, B-C crosslinks may also be present in the residue[14]. In air the boron atoms also form B-O crosslinks from oxygen or water and possibly a B_2O_3 protective film[15,16,17].

Carborane-containing polyesters and polyamides have better thermal properties than their non-carborane analogues as the carborane moiety increases the

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resistance of the ester and amide links to heat[18,19]. However the synthesis of a high molecular weight carborane polymer has hardly ever been achieved[9]. *Meta*-carborane polymers generally have lower viscosities than *ortho*-carborane analogues as the latter are more dense and polar than the former[20]. Apart from being heat resistant, carborane polymers can produce potential high activity, stable "heterogenized" catalysts for hydrogenation of unsaturated hydrocarbons[21,22].

Boron neutron capture therapy (BNCT) is of great interest at present as a cancer treatment, particularly for brain tumours. ^{10}B isotopes absorb neutrons to produce high energy particles capable of destroying local tissue concentrated in tumours[23,24,25].

$$^{10}_{5}B + {}^{1}_{0}n \longrightarrow {}^{11}_{5}B \longrightarrow {}^{7}_{3}Li + {}^{4}_{2}He + 2.28MeV$$

The ^{10}B isotopes need to be in high concentrations in malignant cells though not in surrounding normal tissue for therapy to be effective. Icosahedral carborane derivatives are potential compounds for BNCT due to their high boron content. Carborane-containing biochemical compounds like fatty acids[26], peptides[27], nucleosides[25,28], porphyrins[24,29], macrocycles[30,31] and monoclonal antibodies[23,24] have been made and some could be used for BNCT.

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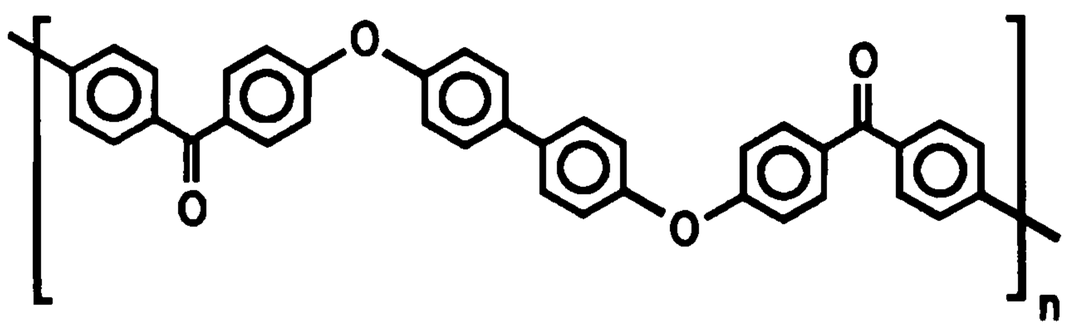
SCOPE OF THIS STUDY

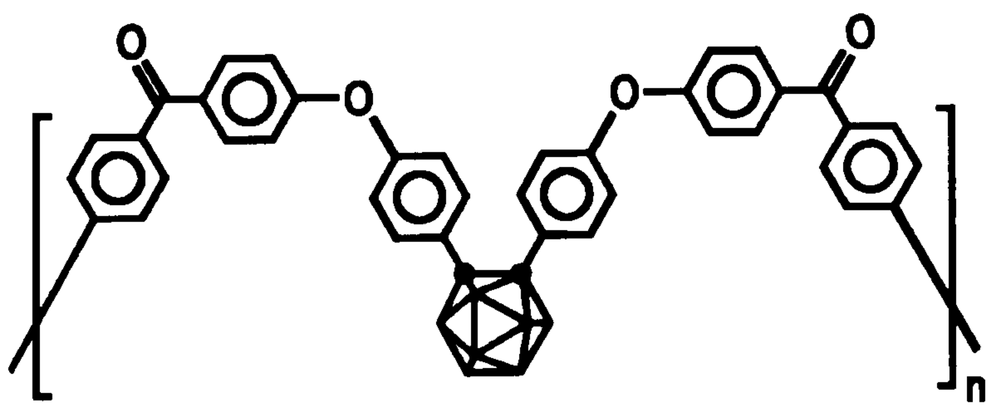
As polyaryletherketones (PEKs) are the most outstanding thermoplastic materials commercially available at present[32,33], carboranes incorporated into these polymers are expected to give even better thermal properties. Four carborane-containing polyaryletherketones (CPEKs) have been produced with better thermal properties, despite lower molecular weights, than the non-carborane analogues[34a]. This study concentrates on producing other suitable carborane monomers which could give CPEKs with better thermal and chemical properties.



A polyaryletherketone[33] (PEK)

Inherent viscosity, η_{inh} = 1.43dLg^{-1}; Softening temperature, T_g = 209°C;

Melting temperature, T_m = 462°C; Weight loss at 800°C = 40%



A carborane-containing polyaryletherketone[34b] (CPEK)

η_{inh} = 0.24dLg^{-1}; T_g = 214°C; T_m = amorphous; Weight loss at 800°C = 5%

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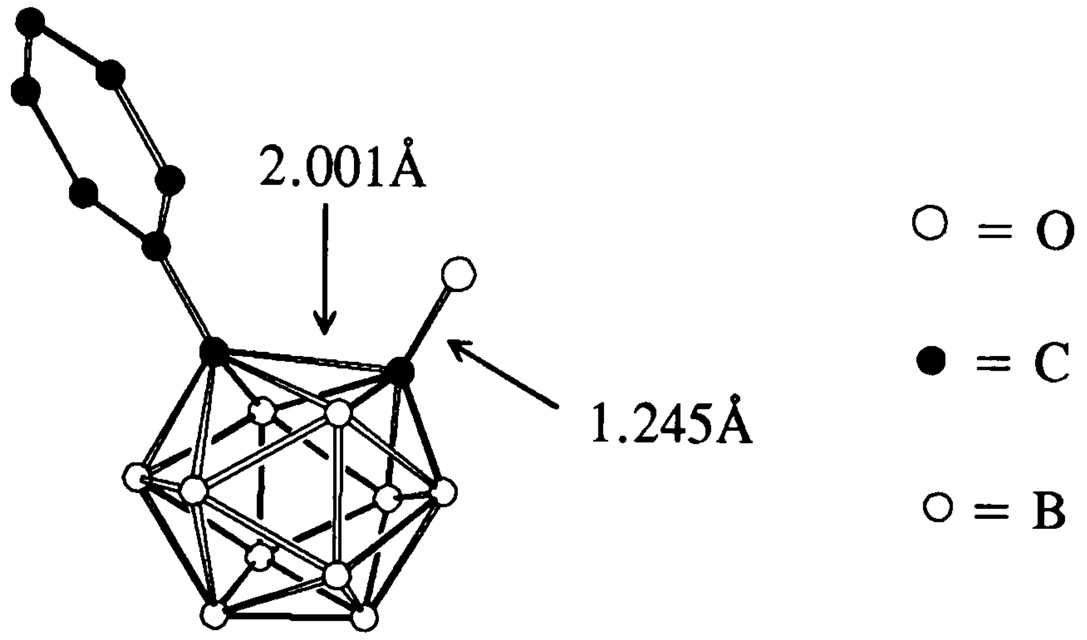
Some carborane derivatives were synthesised in this study to explore the structural effects of substituents, notably those capable of forming exo multiple bonds, as in the *ortho*-carborane anion, $C_6H_5CB_{10}H_{10}CO^-$, below. The latter has a bond length of 2.00 angstroms between the two cage carbons which is the longest known C-C bond as opposed to 1.60-1.70Å found in most carborane derivatives[35].



Hydrogen atoms are omitted for clarity

Chapter 2 is a brief literature review of the nomenclature, formation, bonding and chemical properties of icosahedral carboranes. Techniques used to characterize the carborane derivatives are described in chapter 3.

Chapters 4, 5, 6 and 7 contain the syntheses of some carbon-substituted, boron-iodo, boron-aryl and carbon-aryl carboranes respectively where the aryl carboranes are potential monomers for CPEK formation and chapter 8 describes the carborane derivatives produced for structural study.

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CHAPTER 2

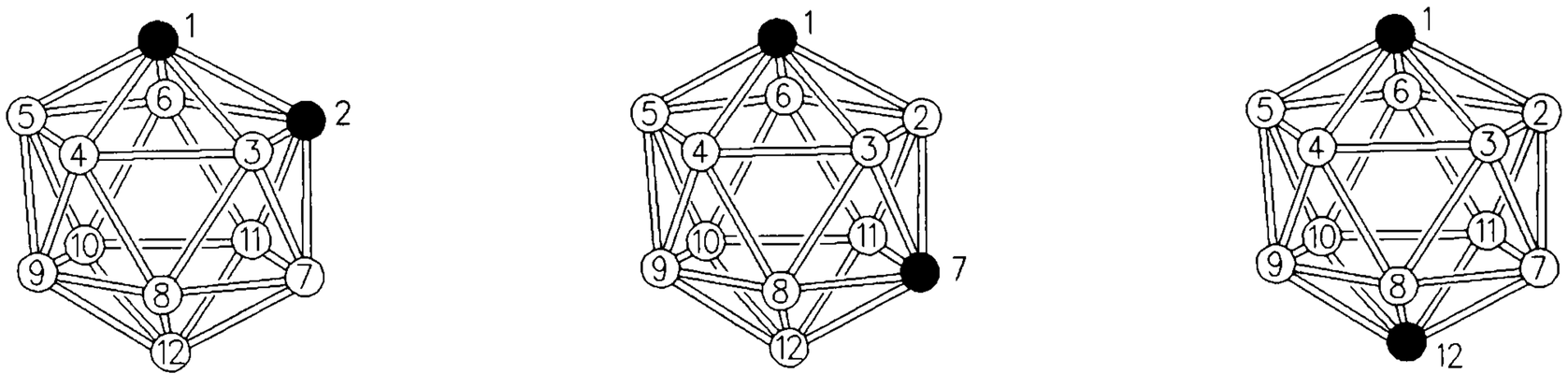
CARBORANES : A GENERAL SURVEY

Nomenclature, formation, isomerization, bonding and chemical properties of icosahedral carboranes are briefly described in this chapter.

NOMENCLATURE OF CARBORANES

The full names of the *ortho*, *meta* and *para* $C_2B_{10}H_{12}$ isomers are 1,2-, 1,7- and 1,12-dicarba-*closo*-dodecaborane(12) respectively. In this thesis *ortho*-, *meta*- and *para*-carboranes are the words used in the text for brevity. The numbering systems and the schematic representations below are adopted.

Numbering systems

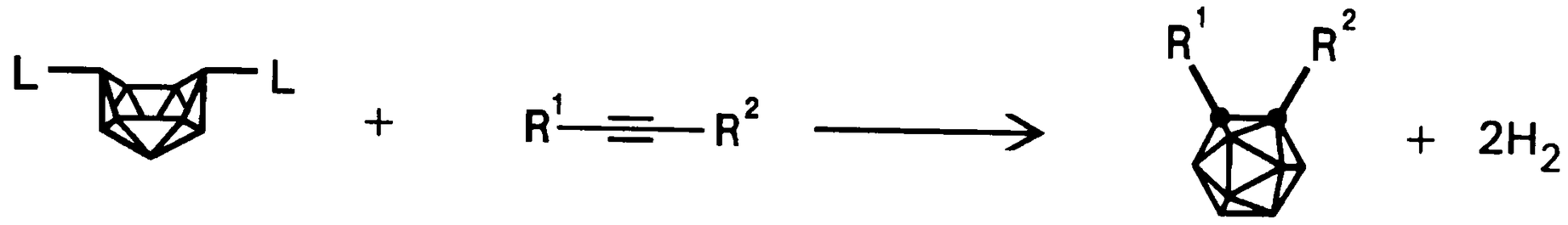


The terminal hydrogen atoms are omitted for clarity.

Schematic representations

FORMATION OF *ORTHO*-CARBORANES

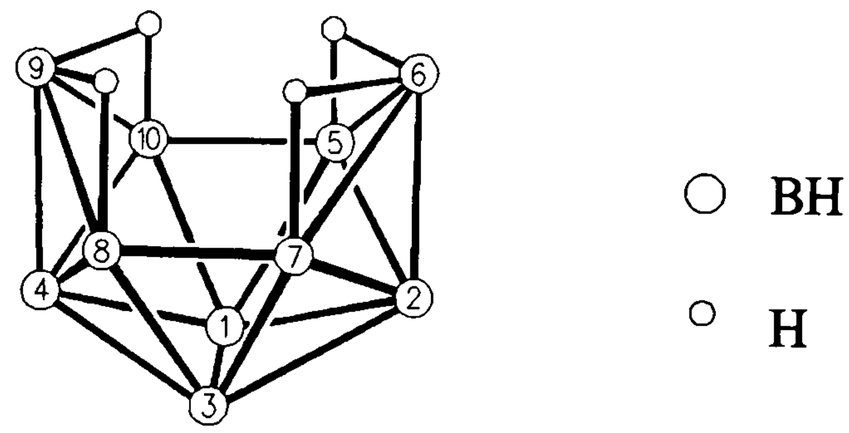
Ortho-carborane and its derivatives can be prepared by reacting a 6,9-bis(ligand)-decaborane, $B_{10}H_{12}L_2$, and suitable acetylenes in a high boiling hydrocarbon solvent like toluene at 40-100°C[1,2,3,4,5].



$B_{10}H_{12}L_2$
L = Lewis base e.g. MeCN

$R^1R^2C_2B_{10}H_{10}$

Decaborane is a neutral boron hydride of formula $B_{10}H_{14}$ with a *nido* structure, an 11-vertex polyhedron with one vacant vertex. Each boron bears a terminal hydrogen and four bridged hydrogens are present along the open face of the molecule[6].



nido-$B_{10}H_{14}$

Decaborane reacts with bases like acetonitrile[7], sulphides, phosphines, dimethylformamide and amines to give an *arachno* diligand decaborane complex, $B_{10}H_{12}L_2$, and hydrogen. The ligands are bonded at the 6 and 9 positions and two hydrogens bridge at the 5,10 and 7,8 positions in the complex. Strong

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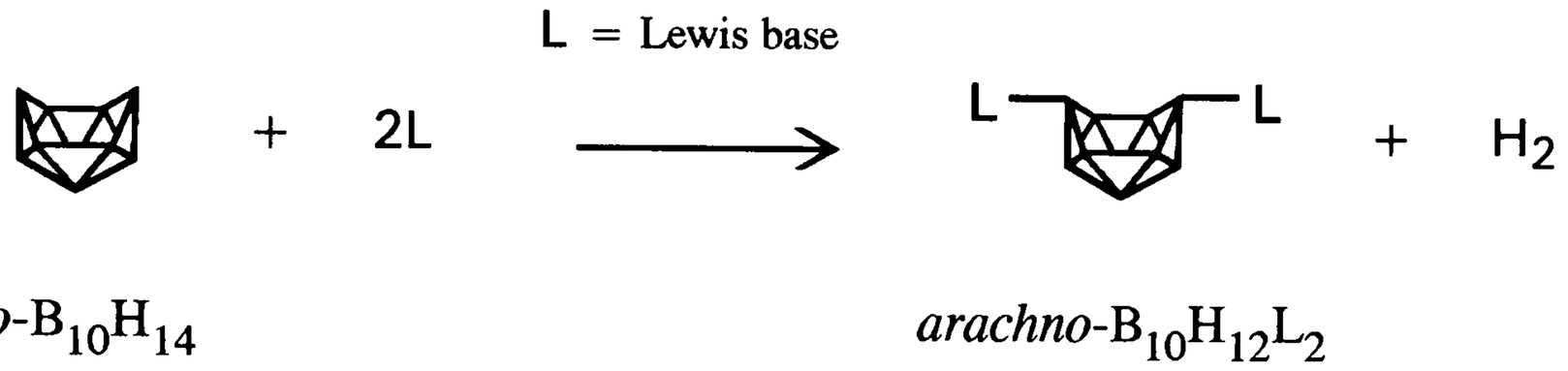
bases, like triethylamine, can give an ionic compound containing a *closo*-decahydrodecaborate dianion, $B_{10}H_{10}^{2-}$, when the decaborane complex is heated[8,9,10]. The ligands of the decaborane complex can be displaced by stronger bases and the order of ligands based on increasing power to displace each other has been determined; the most labile ligands for displacement are alkyl sulphides and acetonitrile[11,12,13]. Decaborane complexes containing these ligands give the best yields of carborane as the ligands are easily removed with suitable acetylenes[14].



Carborane formation was postulated to include a reactive intermediate, a monoligand decaborane complex, $B_{10}H_{12}L$, which was indicated by a study of the kinetics but has not been isolated[15,16]. A compound of molecular formula $B_{10}H_{12}Me_2S$ was isolated[17] by heating $B_{10}H_{12}(Me_2S)_2$ but it is considered to be an exo-substituted decaborane[18], 5-Me_2S-$B_{10}H_{12}$, not the reactive isomer as it reacts very slowly with acetylenes. Partially deuterated decaborane complex, $B_{10}H_{12-x}D_xL_2$, with a suitable acetylene gave deuterium gas indicating that all hydrogen evolved in the synthesis of carboranes from the decaborane complex must originate on the complex[15].

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17. Knoth W.H. Muetterties E.L. *J. Inorg. Nucl. Chem.* 1961 **20** 66-72
18. Thornton-Pett M. Beckett M.A. Kennedy J.D. *J. Chem. Soc. Dalton Trans.* 1986 303-308

Acetylenes containing hydroxy (which degrades the decaborane[1,4,19]), aldehyde, ketone (both are reduced to hydroxy groups during reaction), amino (displaces the labile ligands in the decaborane complex), nitro and cyano (both are reduced to amino) groups are unsuitable for carborane formation[13]. Acetylenes with functional groups attached directly to the C−C triple bond gave very low yields.

Electron-rich acetylenes hydroborate with $B_{10}H_{12}L_2$ much more readily than those containing electron-withdrawing groups. For example, there are low yields of carborane from alkyl acetylenes[2] and no carborane from silyl acetylenes[20] as opposed to high yields from ester, aromatic and halogen-containing acetylenes.

The probable mechanism of carborane formation includes two reactive intermediates, the monoligand decaborane complex and an adduct of monoligand decaborane complex and acetylene[18]. The acetylene acts as a ligand before the carborane is formed. A diagram of the probable mechanism is shown overleaf.

Ortho-carborane and its derivatives can be obtained directly from decaborane and a suitable acetylene in the presence of a Lewis base[3,21] but excess Lewis base reduces the rate of reaction[13]. *Ortho*-carborane is usually prepared in the laboratory from 1,2-bis(hydroxymethyl)- or 1,2-bis(acetoxymethyl)-*ortho*-carborane[22,23] in preference to acetylene and a diligand decaborane complex which requires a rather elaborate apparatus[24] to avoid handling the volatile dangerous acetylene itself.

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22. Grafstein D. Bobinski J. Dvorak J. Smith H. Schwartz N. Cohen M.S. Fein M.M. *Inorg. Chem.* 1963 **2** 1120-1125
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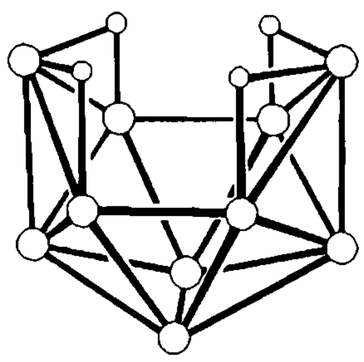
PROBABLE MECHANISM OF CARBORANE FORMATION[18]

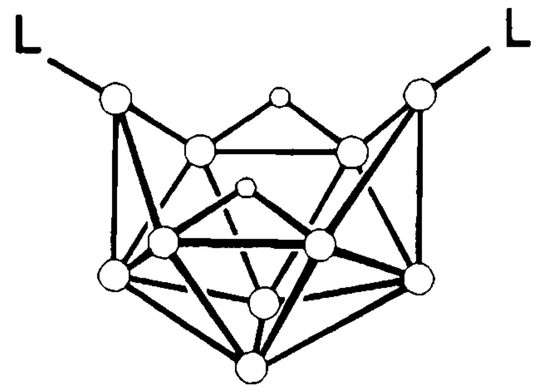


$B_{10}H_{14}$

L = R_2S, RCN, R_3P or R_3N

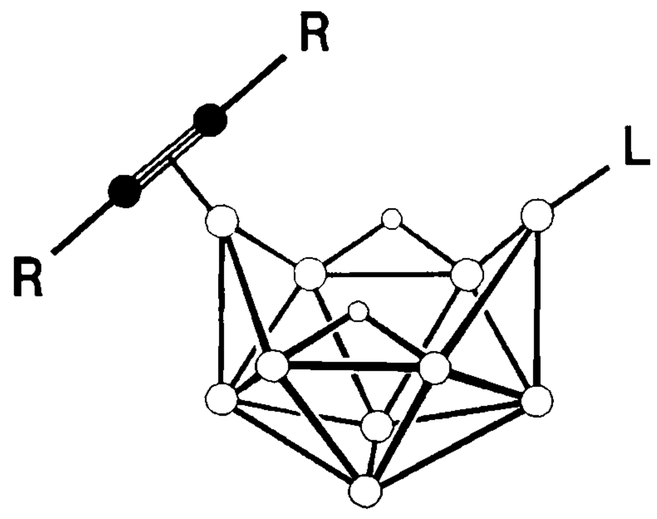
$\longrightarrow$

$- H_2$



○ H ○ BH

● C ⊘ B

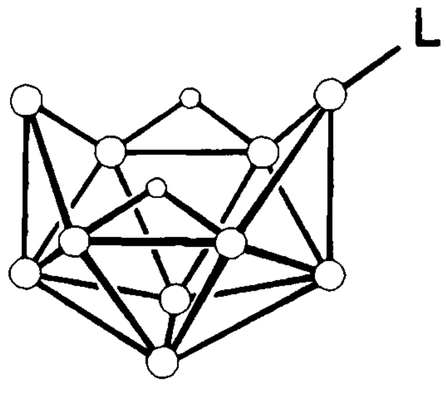


(not isolated)

R — R

$\longleftarrow$

No OH, CN, NH_2, NO_2, aldehyde and ketone groups present in R

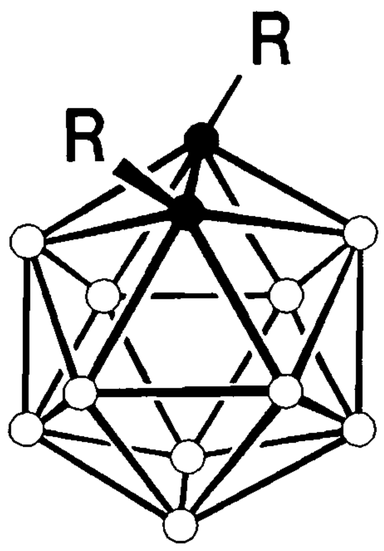


(not isolated)

$\Rightleftharpoons$

+ L

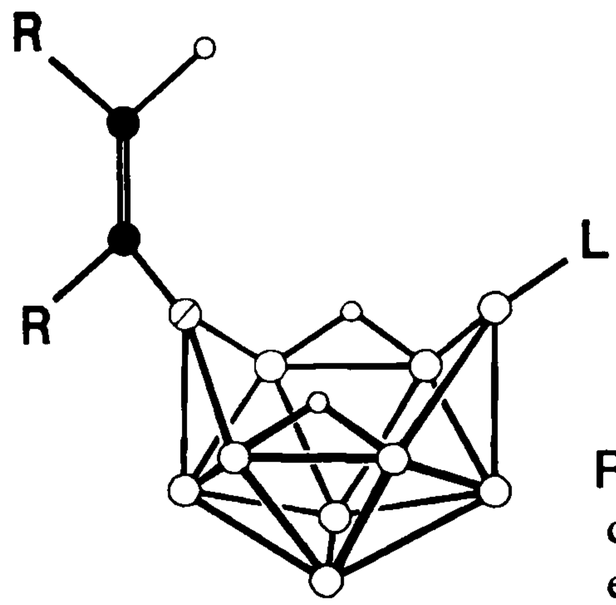
$\downarrow$



$R_2C_2B_{10}H_{10}$

R = electron-withdrawing group e.g. aryl, halogen- and ester-containing alkyl; alkyl groups give low yields.

$\searrow$



R = electron-donating group e.g. SiR_3, alkyl.

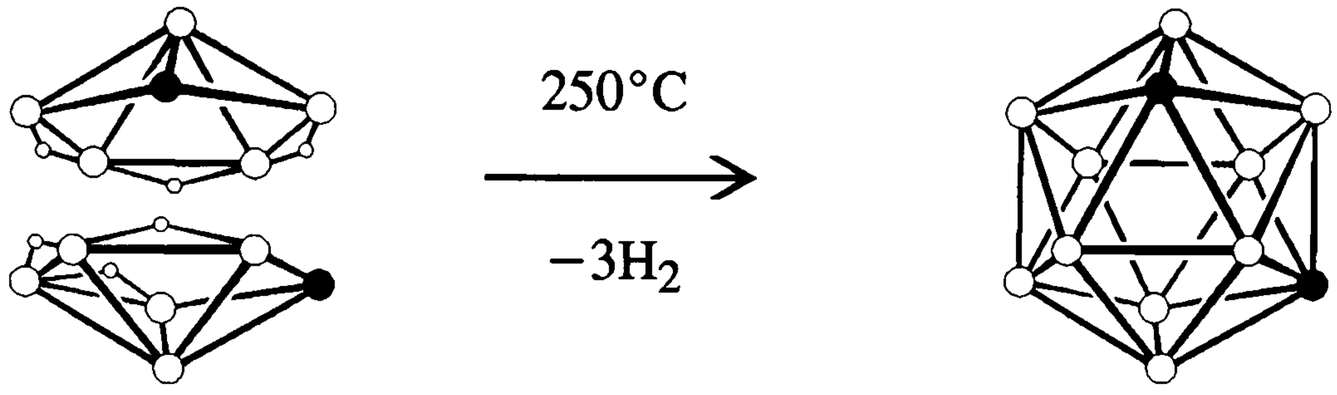
(not isolated)

$\downarrow$

Hydroborated products.

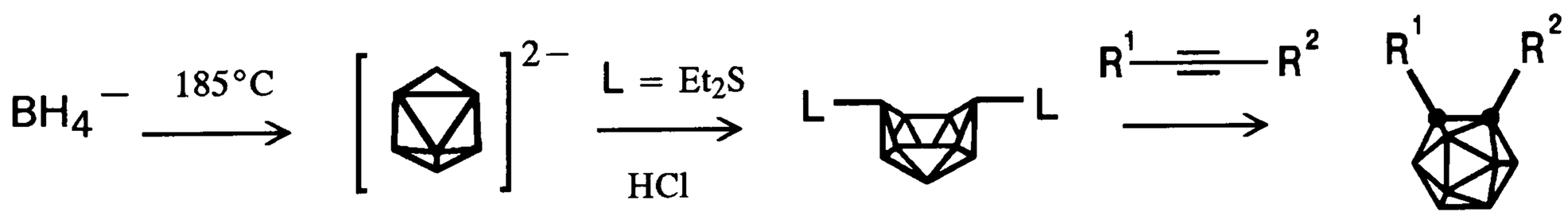
ALTERNATIVE ROUTES TO CARBORANE FORMATION

Meta-carborane can be produced by a direct synthesis from decaborane and acetylene at 700°C[25] or from the *nido*-carborane CB_5H_9 at 250°C[26].



2 *nido*-CB_5H_9 *meta* $C_2B_{10}H_{12}$

Diphenyl-*ortho*-carborane has been made from decaborane and diphenylacetylene in the presence of cobalt and cyclopentadiene[27]. The formation[28] of 6,9-bis(diethylsulphide)-decaborane complex, $B_{10}H_{12}(SEt_2)_2$, from the decahydrodecaborate dianion, $B_{10}H_{10}^{2-}$, indicates that toxic decaborane can be avoided in carborane syntheses from simple borohydrides[29].



$B_{10}H_{10}^{2-}$ $B_{10}H_{12}(Et_2S)_2$ $R^1R^2C_2B_{10}H_{10}$

25. Ditter J.F. Klusmann E.B. Oakes J.D. Williams R.E. *Inorg. Chem.* 1970 **9** 889-892
26. Rietz R.R. Hawthorne M.F. *Inorg. Chem.* 1974 **13** 755-756
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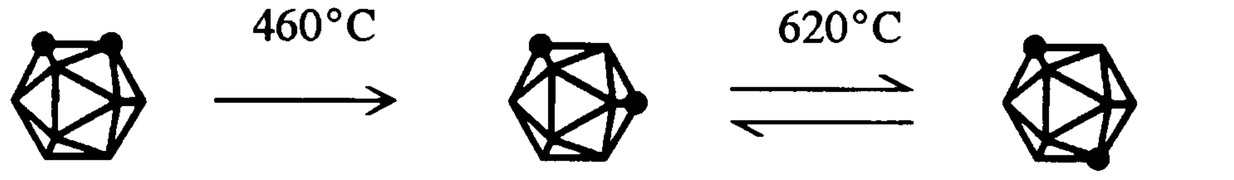
29. Makhlouf J.M. Hough W.V. Hefferan G.T. *Inorg. Chem.* 1967 **6** 1196-1198

ISOMERIZATION OF CARBORANES

Meta-carborane is obtained quantitatively by thermal rearrangement from *ortho*-carborane at 460°C for 24 hours[30], in an autoclave at 700°C for one hour[31] or in a heated tube at atmospheric pressure and 600°C for 0.5 minutes[32]. *Para*-carborane is produced from *meta*-carborane at 620°C for eight hours[33], from *ortho*-carborane in an autoclave at 700°C for 12 hours[31,34] or in a heated tube at atmospheric pressure and 700°C for 0.3 minutes. The *para*-carborane product from thermal rearrangement is accompanied by *meta*-carborane, bicarboranes[31,35,36] and large amounts of decomposed products[33]. It has been shown that the isomerization of *meta* to *para* isomer is reversible at 620-700°C with the equilibrium mixture approximately 55 : 45 *meta* : *para*[31,32,37,38].



$1,2\text{-}C_2B_{10}H_{12}$ $1,7\text{-}C_2B_{10}H_{12}$ $1,12\text{-}C_2B_{10}H_{12}$

Thermal isomerisation of carborane derivatives has shown that the temperature required for conversion from *ortho* to *meta* is usually lower than for parent carboranes. Bulky groups attached to the carbon atoms were shown to lower the temperature probably due to steric, not electronic, effects[39]. Replacing hydrogen atoms attached to carboranyl boron by chlorine atoms also lowers the isomerization temperature to 300°C[40]. Isomerization of carboranes with a functional organic substituent is generally unsatisfactory[30].

Meta-carborane and its phenyl-substituted derivatives also undergo rearrangement via dianions, $R_2C_2B_{10}H_{10}^{2-}$, to their *ortho* derivatives at ambient

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30. Grafstein D. Dvorak J. *Inorg. Chem.* 1963 **2** 1128-1133
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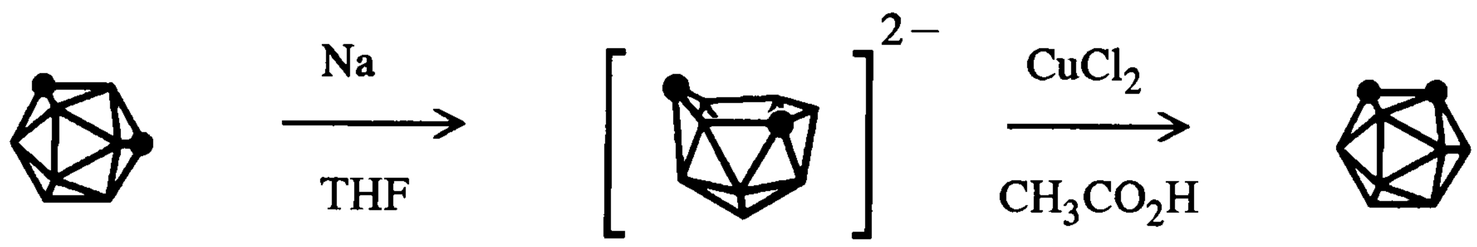
39. Salinger R.M. Frye C.L. *Inorg. Chem.* 1965 **4** 1815-1816
40. Stanko V.I. Klimova A.I. *J. Gen. Chem. U.S.S.R.* 1966 **36** 450-453

temperatures[41]. The dianions are formed from neutral carboranes by an alkali metal in tetrahydrofuran (THF) or liquid ammonia[42]. The dianions themselves showed no evidence of rearrangement so it was concluded that the isomerization process occurs during the oxidation of the dianion[43,44]. *Meta*- and *para*-carborane derivatives containing a methyl or halogen substituent gave parent *ortho*- or *meta*-carborane[38] via the redox isomerization indicating the carborane dianion to be fundamentally different from neutral carborane[45]. Addition of two electrons leads to a considerable rearrangement of the geometrical structure and electronic shell of the molecule resulting in a new system of bonding orbitals[42,44]. Protonation of the dimethyl-*ortho*-carborane dianion gave two isomers containing *nido*-carborane structures. An X-ray study[46] of the unstable isomer structure showed a CB_3 quadrilateral face, instead of two triangular faces, on the carborane cage. The structure of the fluxional carborane dianion has not been determined.



The red cobalt complex produced from cyclopentadienyl anion, *ortho*-carborane dianion and cobalt chloride in tetrahydrofuran was found to be fluxional in solution at 20°C[47] and its structure by X-ray analysis[48] contained a *nido*-carborane ligand with two CB_3 quadrilateral faces. The carborane ligand in this complex undergoes thermal rearrangement at 60°C and the product rearranges again at 100°C to give two complexes with different carborane ligands[49]. Iron (II), nickel (II) and cobalt (III) complexes containing two carborane ligands also had

41. Zakharkin L.I. Kalinin V.N. Podvisotskaya L.S. *Bull. Acad. Sci. U.S.S.R. Chem. Div.* 1967 2212-2217
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47. Dustin D.F Dunks G.B. Hawthorne M.F. *J. Am. Chem. Soc.* 1973 **95** 1109-1115
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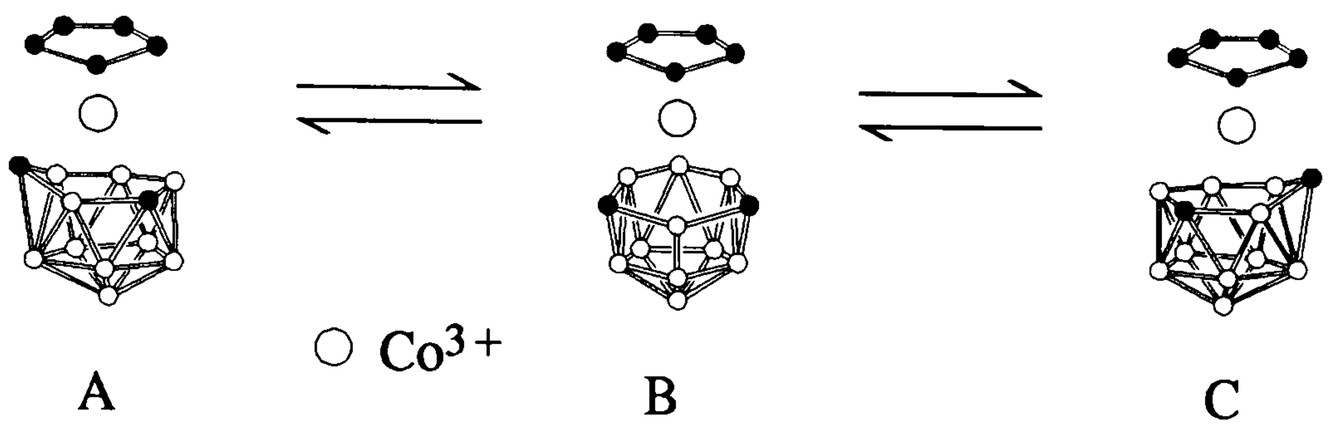
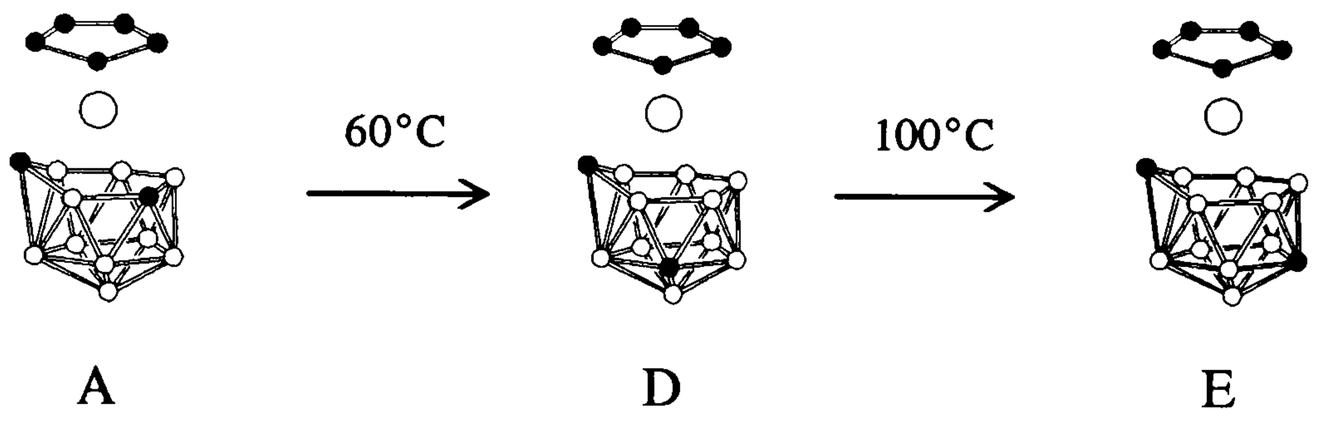
49. Dunks G.B. McKown M.M. Hawthorne M.F. *J. Am. Chem. Soc.* 1971 **93** 2541-2543

fluxional behaviour[46] and oxidation of these complexes gave a mixture of *ortho*-, *meta*- and *para*-carboranes[44]. A mechanism different from the uncomplexed redox isomerization is likely to occur in this carborane isomerization[37].

1.

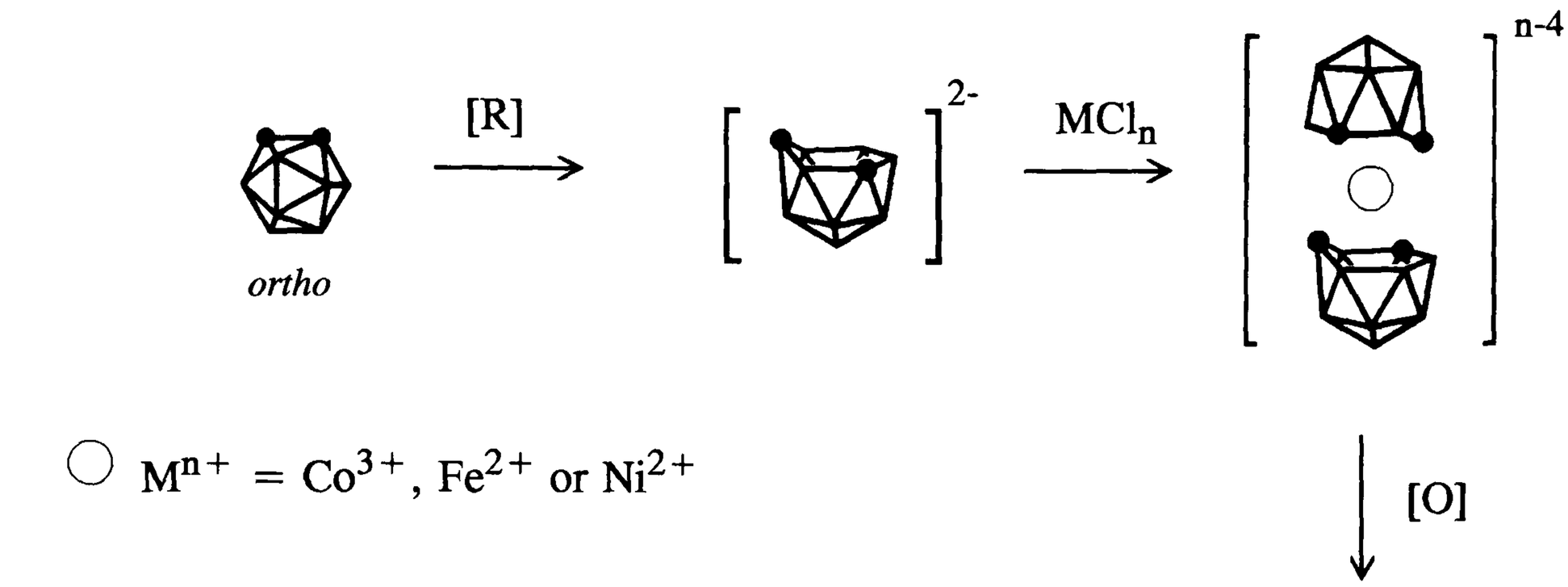


2.



Fluxional behaviour at 20°C (1) and thermal rearrangements (2) of $(C_5H_5)Co(C_2B_{10}H_{12})$ complex. Structure B was observed by X-ray studies.

There are many theories of the mechanism of icosahedral carborane rearrangements which are described in detail in Appendix A.



Complexed redox isomerization

BONDING IN CARBORANES

Icosahedral carboranes are 'electron-deficient' in the sense that there are more valence or atomic orbitals (60) than electrons (50) but three-centre two-electron bonds make possible a simple description of them as molecules with filled localized orbitals[50]. However there is no unique arrangement of the thirteen skeletal bonds (three 2c2e BB, BC or CC bonds and ten 3c2e BBB, BBC or BCC bonds) that are required to involve each skeletal atom in three skeletal bonds. The bonding orbitals of the $C_2B_{10}H_{12}$ icosahedral framework are best explained using molecular orbital theory rather than the localized bond (*styx*) theory as high symmetry is present in the molecule[49,51]. Each carbon and boron atom contributes one *s* and three *p* atomic orbitals (A.O.s)[52]. An *sp* hybrid orbital is assumed to bond the terminal hydrogen which leaves an *sp* hybrid orbital pointing radially inwards and two *p* orbitals tangential to the pseudospherical surface of the cluster[50]. In total there are 12 radial *sp* hybrid and 24 tangential *p* A.O.s available for skeletal bonding. From molecular orbital calculations there are 13 bonding and 23 antibonding skeletal molecular orbitals[51]. Each bonding orbital requires an electron pair so a total of 26 electrons is required. These are provided by the C-H (3 electrons per unit) and B-H (2 electrons) units[53]. A different and simplified approach to cage bonding is tensor surface harmonic theory which treats the cluster framework as a perturbed spherical shell with its surface vector harmonics as molecular orbitals[54,55,56,57].

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50. Lipscomb W.N. *Science* 1977 **196** 1047-1055
51. Wade K. *Adv. Inorg. Radiochem.* 1976 **18** 1-66
52. Longuet-Higgins H.C. Roberts M.de V. *Proc. Roy. Soc., Ser. A* 1955 **230** 110-119
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54. Stone A.J. *Mol. Phys.* 1980 **41** 1339-1354
55. Stone A.J. *Inorg. Chem.* 1981 **20** 563-571
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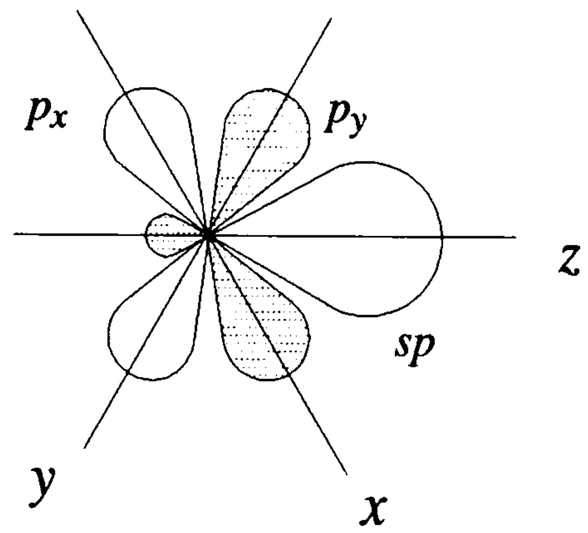
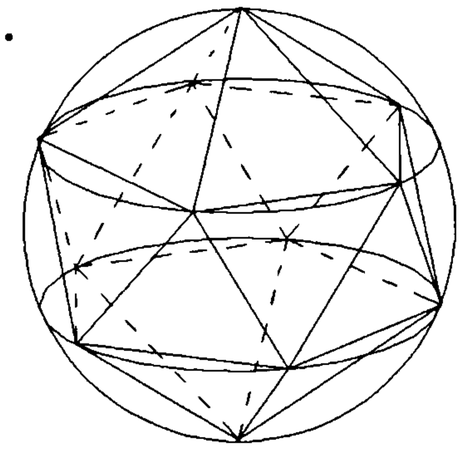
57. Stone A.J. *Polyhedron* 1984 **3** 1299-1306

Atomic orbitals of a boron or carbon atom involved in skeletal bonding.
The *z*-axis passes through the centre of the cage.

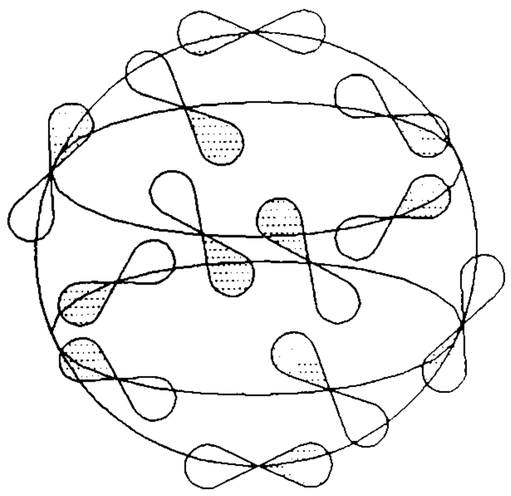


The surface bonding *p*-orbitals are best visualised using the icosahedron cage as a perturbed sphere (A). Two types of surface *p*-orbital bonding in the icosahedral framework are shown below (B and C).

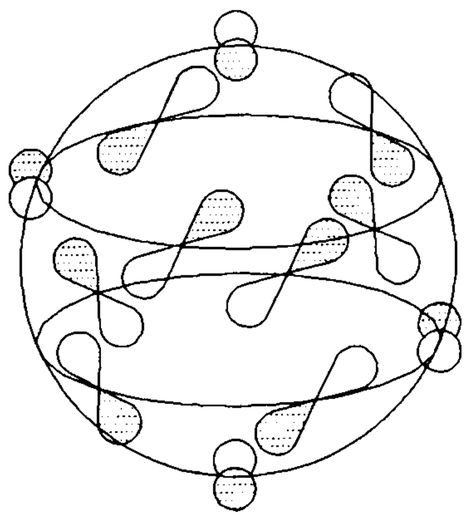
A.



B.



C.



Predictions of molecular structures, reactivities, stabilities, charge distributions, molecular structures, dipole moments, molecular energies and ionization potentials on the icosahedral isomers have been made using molecular orbital calculations particularly EHMO[58], NEMO[59], CNDO[60], MOBI[61], INDO[62], PRDDO[63] and MNDO[64]. He I photoelectron spectra[65] and photoelectron mass spectra[66] of the parent carboranes, *ortho* and *meta*, gave ionization potentials which correspond well with molecular orbital energy calculations. The structures and stabilities of $C_2B_{10}H_{12}$ isomers have also been predicted using valence rules[67], the six electron rule[68] and the topological charge stabilization rule[69].

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58. EHMO = extended Huckel molecular orbital: Hoffman R. Lipscomb W.N. *J. Chem. Phys.* 1962 **36** 3489-3493
59. NEMO = non-empirical molecular orbital: Koetzle T.F. Lipscomb W.N. *Inorg. Chem.* 1970 **9** 2743-2748
60. CNDO = complete neglect of differential overlap: Cheung C-C.S. Beaudet R.A. Segal G.A. *J. Am. Chem. Soc.* 1970 **92** 4158-4164
61. MOBI = molecular orbital bond index: Armstrong D.R. Perkins P.G. Stewart J.J.P. *J. Chem. Soc. Dalton Trans.* 1973 838-840; Stephenson I.R. Ph.D. Thesis University of Durham Durham 1988 p220
62. INDO = intermediate neglect of differential overlap: Guest M.F. Hillier I.H. *Mol. Phys.* 1973 **26** 435-452
63. PRDDO = partial retention of diatomic differential overlap: Dixon D.A. Kleier D.A. Halgren T.A. Hall J.H. Lipscomb W.N. *J. Am. Chem. Soc.* 1977 **99** 6226-6237
64. MNDO = modified neglect of differential overlap: Dewar M.J.S. McKee M.L. *Inorg. Chem.* 1980 **19** 2662-2672
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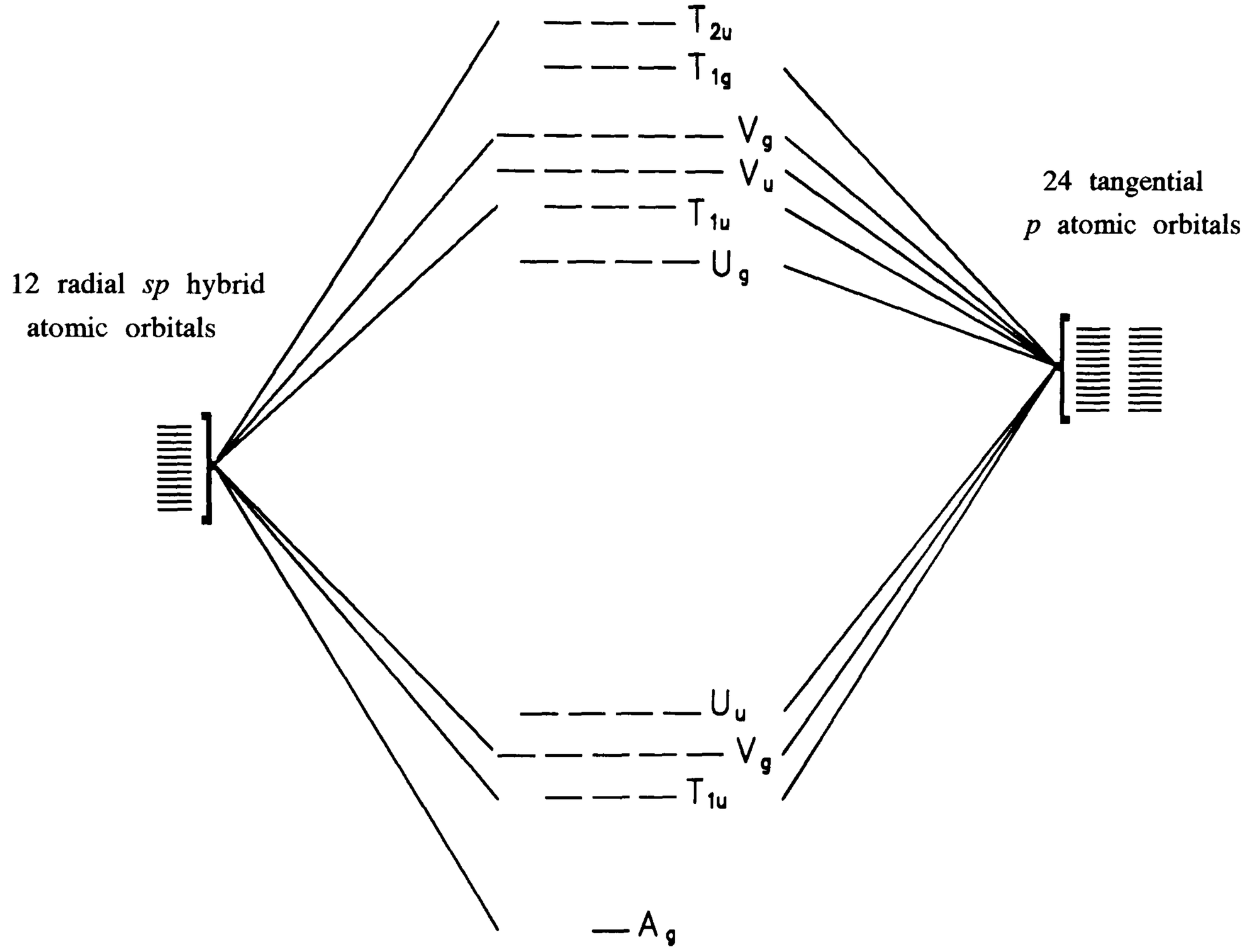
67. Williams R.E. *Adv. Inorg. Radiochem.* 1976 **18** 67-142
68. Jemmis E.D. *J. Am. Chem. Soc.* 1982 **104** 7017-7020
69. Ott J.J. Gimarc B.M. *J. Am. Chem. Soc.* 1986 **108** 4303-4308

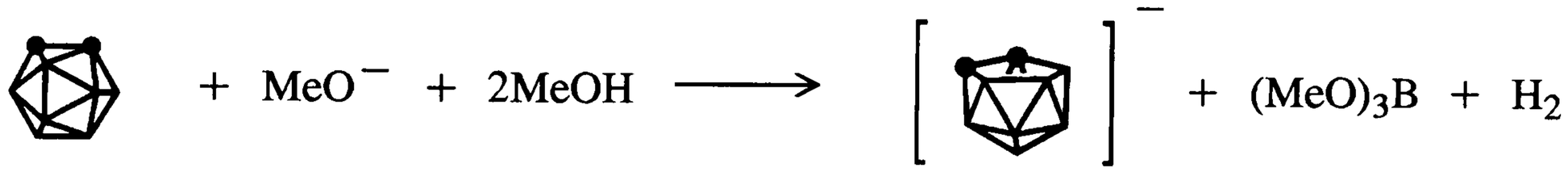


Molecular orbital energy diagram of the icosahedral skeleton[51].

CHEMICAL PROPERTIES OF CARBORANES

$C_2B_{10}H_{12}$ isomers have a nearly regular C_2B_{10} icosahedral cage with B-B bond lengths of approximately 1.77Å, B-C 170Å and, for the *ortho* isomer, C-C 164Å[70,71]. The skeletal bonding in these carboranes involves cage electron delocalization with a "closed shell" of filled bonding orbitals giving them 'pseudo-aromatic' properties. The carborane skeleton is thermally very stable, compared to neutral *nido* and *arachno* boron hydrides, and can withstand temperatures up to 700°C[72]. The thermal stability increases from *ortho*- then *meta*- to *para*-carborane[73,74].

The cage is unaffected by oxidizing agents like chromic acid[71] and reducing agents like lithium aluminium hydride[75]. However it is degraded by strong Lewis bases like alcoholic alkali[76,77] and amines[74,78,79,80]. The rate of degradation decreases from *ortho* to *para*[81] and controlled degradation has been used to remove the unwanted *ortho* isomer in a mixture of *ortho*- and *meta*-carborane derivatives giving only the *meta* isomer[82].



1,2-$C_2B_{10}H_{12}$ *nido* 7,8-$C_2B_9H_{12}^-$

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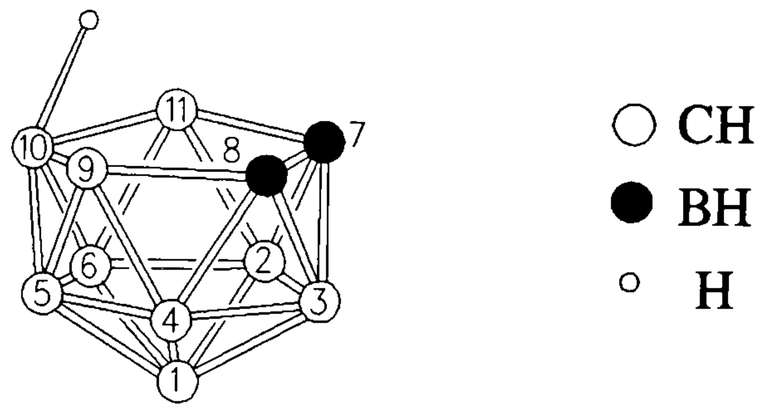
Dicarba-*nido*-undecaborate (-1) anion, $C_2B_9H_{12}^-$, is formed by base degradation of carborane where the relatively positive boron atom (3 or 6 position in *ortho*-carborane) is removed[78,79,80,81]. X-ray structural study[83] of the *nido*-7,8-$C_2B_9H_{12}^-$ anion showed two hydrogens bonded to B(10) not the hydrogen bridged to B(10) and B(9) or B(11) assumed in earlier literature[84]. The $C_2B_9H_{12}^-$ anion can be deprotonated by sodium hydride to form a *nido*-$C_2B_9H_{11}^{2-}$ anion which is the precursor for many metallocarboranes. Its open face is structurally and electronically equivalent to the pentahaptocyclopentadienide anion, $C_5H_5^-$, present in many transition metal compounds.



Structure of *nido*-$C_2B_9H_{12}^-$

Carboranyl carbon atoms in the icosahedral cage are positively charged compared to boron atoms so the C-H group is weakly acidic[85]. The acidity decreases from *ortho* to *meta* then *para* as the magnitude of the positive charge on the cage carbons decreases in the same order[86,87,88,89].

All carborane isomers can be metallated at the acidic carboranyl C-H group by alkali metal amides in liquid ammonia[81,87,90,91] or by organolithium[74,86,92,93] and alkylmagnesium reagents[94]. The metallated carboranes

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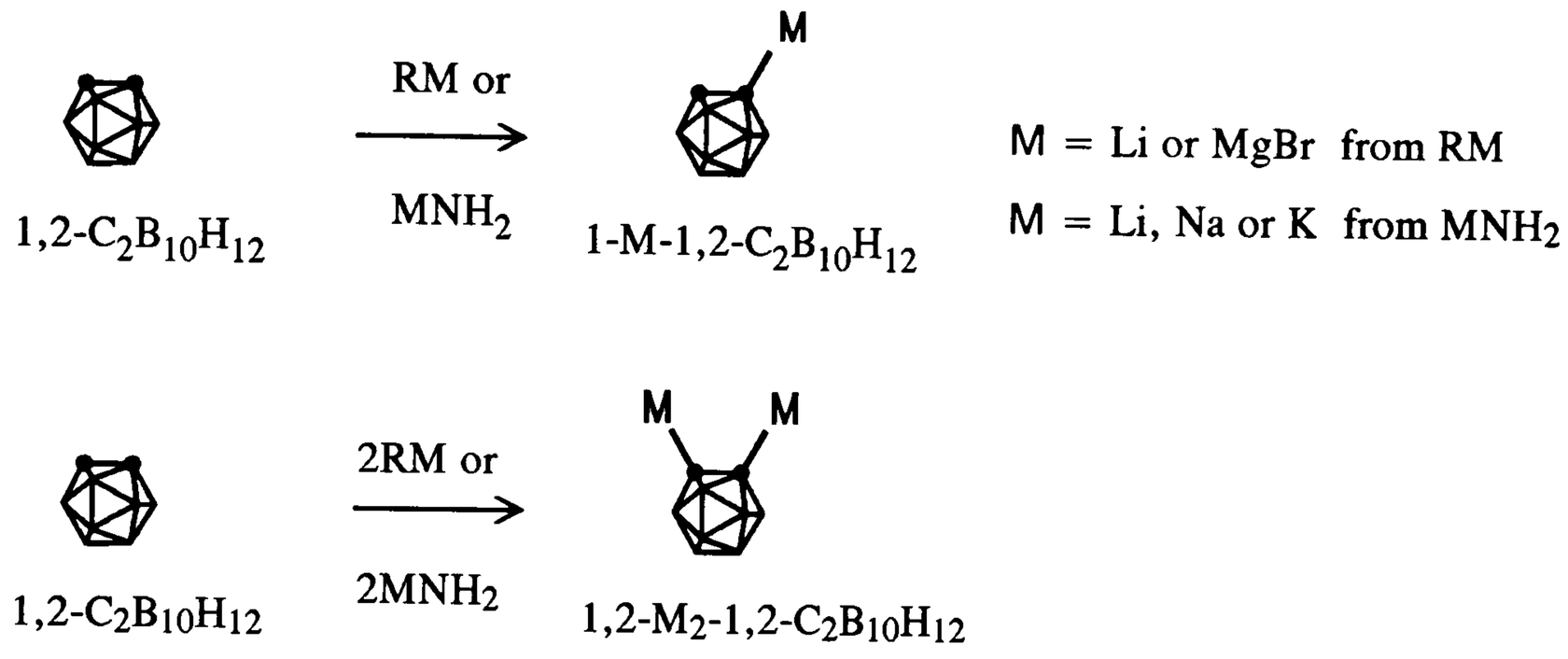
92. Stanko V.I. Klimova A.I. Kashin A.N. *J. Gen. Chem. U.S.S.R.* 1969 **39** 1857

can then form many carbon-substituted derivatives with appropriate organic halides and metal halides. For monosubstituted carborane formation the type of solvent is important as equilibrium exists between the mono- and di-metallated carboranes in some solvents[93,95,96,97].



C-metallation of *ortho*-carborane

Boron-substituted carboranes can be formed from parent carboranes by electrophilic reagents, by radicals generated photochemically or via the dianion of the parent carborane. The rates of reaction with electrophiles decrease in the order *ortho*, *meta* and *para* as the charge at the most negatively charged boron atom of these isomers decreases. Controlled chlorination has been used to separate the *para*-carborane from *meta*-carborane in a mixture of these isomers[108]. Deuterium-hydrogen exchange occurs at B-H bonds with deuterium gas and transition metal catalysts[98,99,100]. The exchange was found to proceed regioselectively with some catalysts e.g. at B(3) in preference to B(9).

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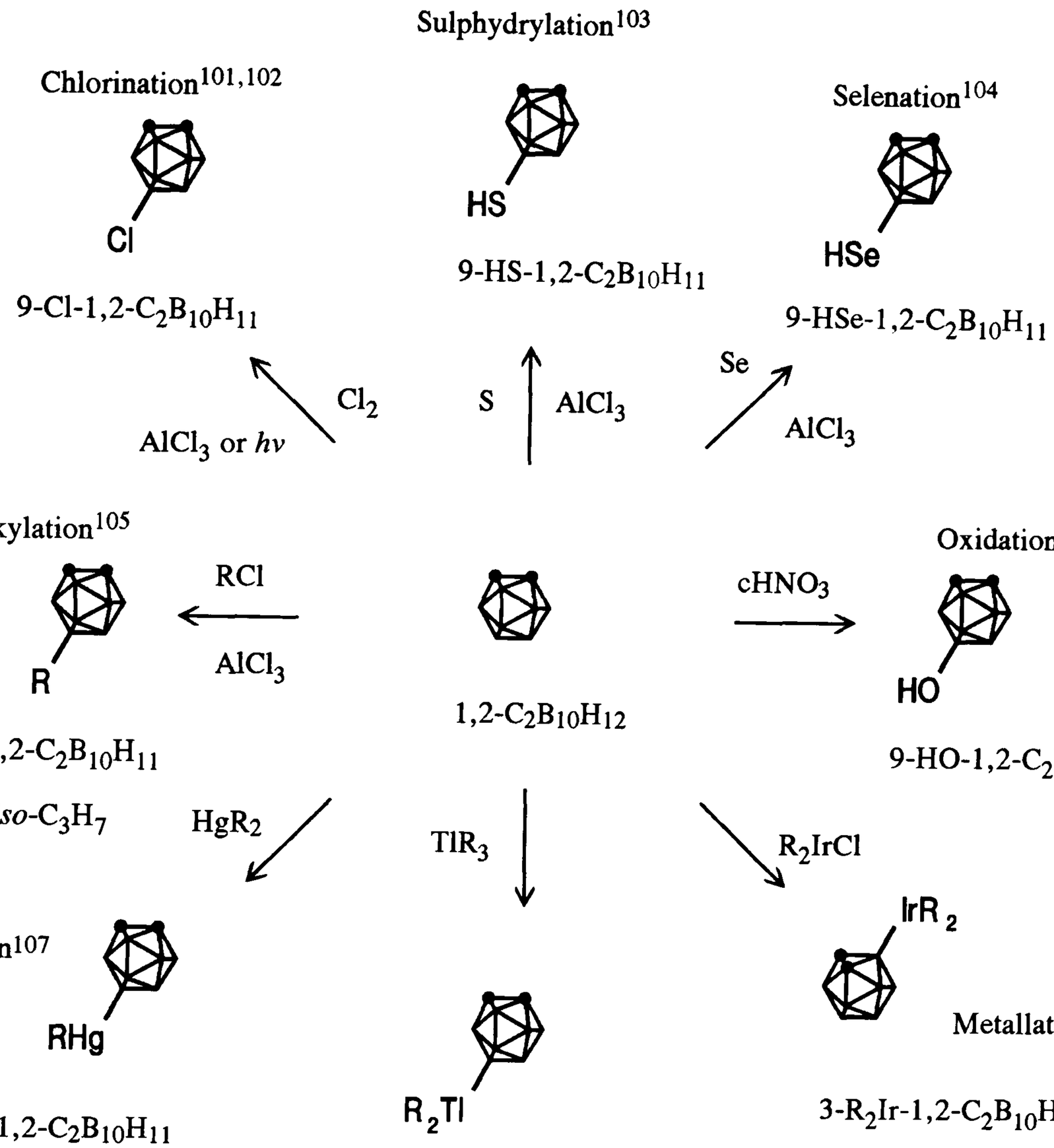

Some boron-substituted carboranes preparable from *ortho*-carborane

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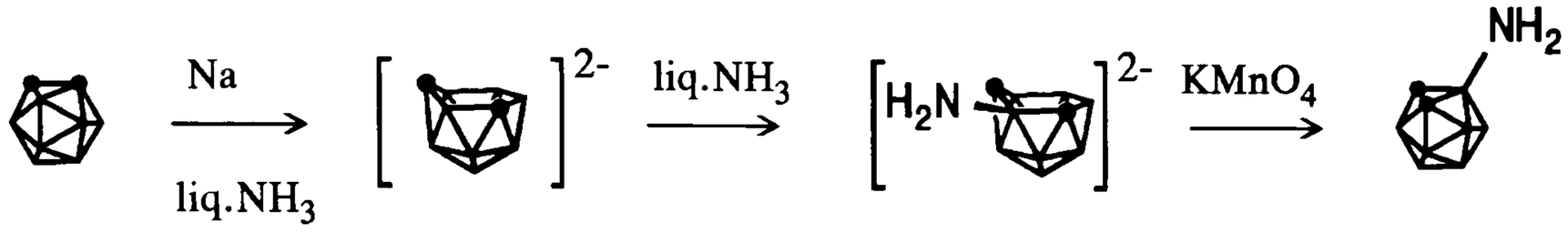
Amination via carborane dianion[109]



$1,2\text{-}C_2B_{10}H_{12}$ $C_2B_{10}H_{12}^{2-}$ $C_2B_{10}H_{11}(NH_2)^{2-}$ $3\text{-}NH_2\text{-}1,2\text{-}C_2B_{10}H_{11}$

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CHAPTER 3

TECHNIQUES USED IN CARBORANE CHARACTERIZATIONS

This chapter describes the different techniques used in this study to characterise the carborane derivatives produced. The techniques used are infrared spectroscopy, mass spectroscopy, nuclear magnetic resonance spectroscopy (^{1}H, ^{11}B, ^{13}C, ^{19}F solution state and ^{13}C solid state), X-ray crystallography, ultraviolet spectroscopy, elemental analysis and gas chromatography.

INFRARED SPECTROSCOPY

Infrared (I.R.) spectroscopy is a useful tool for characterizing carborane derivatives as it shows characteristic bands of the carborane cage along with bands of organic functional groups, if any, present in the carborane derivative.

All carborane derivatives produced in this study are air-stable solids and a sample suitable for I.R. spectroscopy can be produced as a nujol mull, as the neat solid or as a potassium bromide pellet. Nujol is only used for solids that decompose during KBr disc formation. I.R. spectra were carried out on a Perkin Elmer PE377 Grating Infrared Spectrophotometer with range 4000-400cm^{-1}.

The near icosahedral geometry of *ortho*- and *meta*-carborane is expected to give complex infrared spectra as there are 53 normal I.R. vibrations present in each molecule[1]. However I.R. spectra of these carboranes show only 15-20 bands and some bands have been assigned to certain vibrations with the help of other I.R. spectra of carborane derivatives, and of the Raman spectra of parent carboranes and C-deuterated *para*-carborane.

The carboranyl C-H stretching vibrations, νC-H, give a characteristically sharp band at approximately 3050cm^{-1}. The high frequency of carboranyl νC-H with respect to other νC-H observed in alkyl and aryl compounds is due to the strong electron-acceptor effect in carboranes[2]. Both antisymmetric, νC-H_{as}, and symmetric, νC-H_s, vibrations of parent carboranes have the same frequencies from detailed I.R. and Raman studies which indicate that, even in *ortho*-carborane, the two νC-H vibrations are independent of each other[3]. The presence of two C-H stretching bands in I.R spectrum of any substituted carborane signifies chemical nonequality of the two C-H bands in the given molecule. The C-H bands have been found to depend on intramolecular and intermolecular interactions. The intensity of the νC-H band increases with increasing electron-withdrawing substituents on one of the carbons in *ortho*-carborane[4]. In proton-acceptor solvents parent carboranes showed broad νC-H bands indicating hydrogen

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1. Leites L.A. Vinogradova L.E. Bukalov S.S. Aleksanyan V.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1975 492-496
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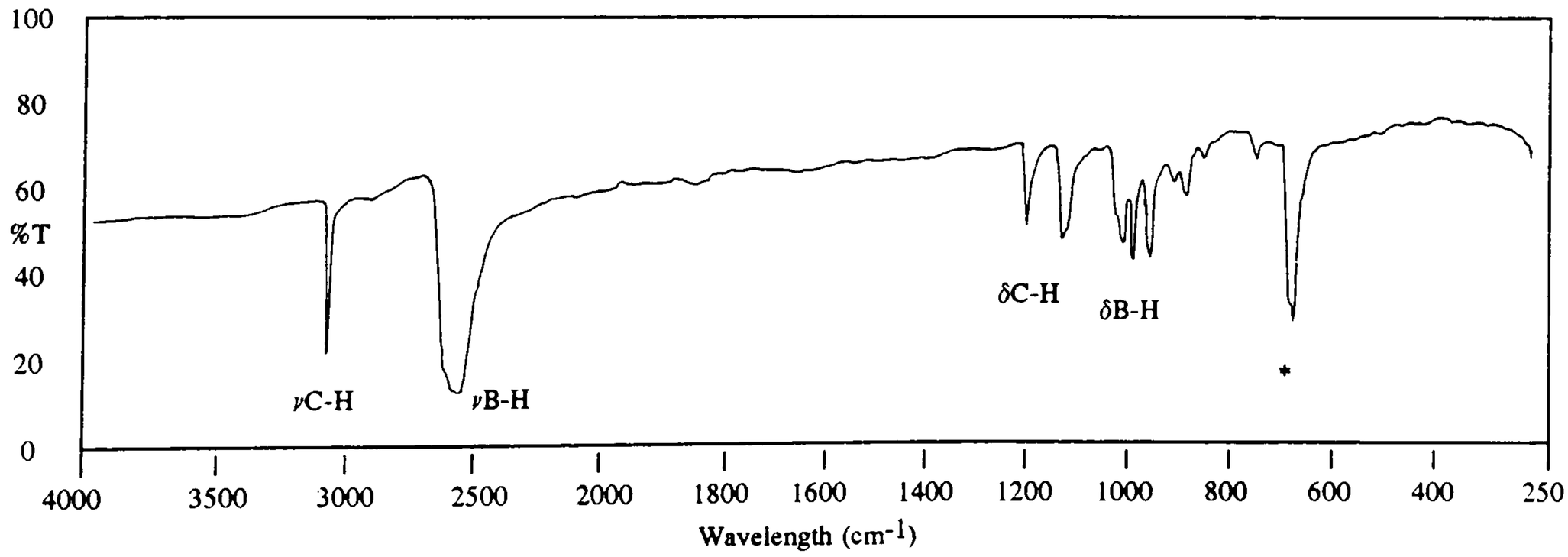
bonding[5]. I.R. spectra of adducts formed from decachlorocarboranes, $RCB_{10}Cl_{10}CH$, and bases give very broad νC-H bands in the 2850-2650cm^{-1} region[6].

B-H stretching vibrations are usually very strong and broad at approximately 2600cm^{-1} in carboranes. The νB-H frequency depends on the C-attached substituents, increasing with halogens and decreasing with metal atoms[7]. The fine structure in the νB-H band is usually seen with bulky substituted groups like iodo and phenyl[2]. Other I.R. active vibrations of carboranes assigned are the C-H and B-H bending (δ) vibrations at 1250-1150cm^{-1} and 1050-980cm^{-1} respectively. A difference between *ortho*- and *meta*-carborane derivatives occurs in their δC-H bands where the 1220cm^{-1} band is only seen in *ortho*-carborane and its derivatives. A strong band at approximately 720cm^{-1} is present in all carborane I.R. spectra and has been assigned to an antisymmetric cage stretching vibration[7]. The νB-Cl vibrations are observed at 1100-1000cm^{-1} in decachlorocarboranes. Carboranes containing B-I bonds usually show strong bands in the 900-700cm^{-1} region corresponding to νB-I vibrations.

Infrared spectrum of *ortho*-carborane, o-$C_2B_{10}H_{12}$ (KBr disc; cm^{-1})



* = antisymmetric cage vibration

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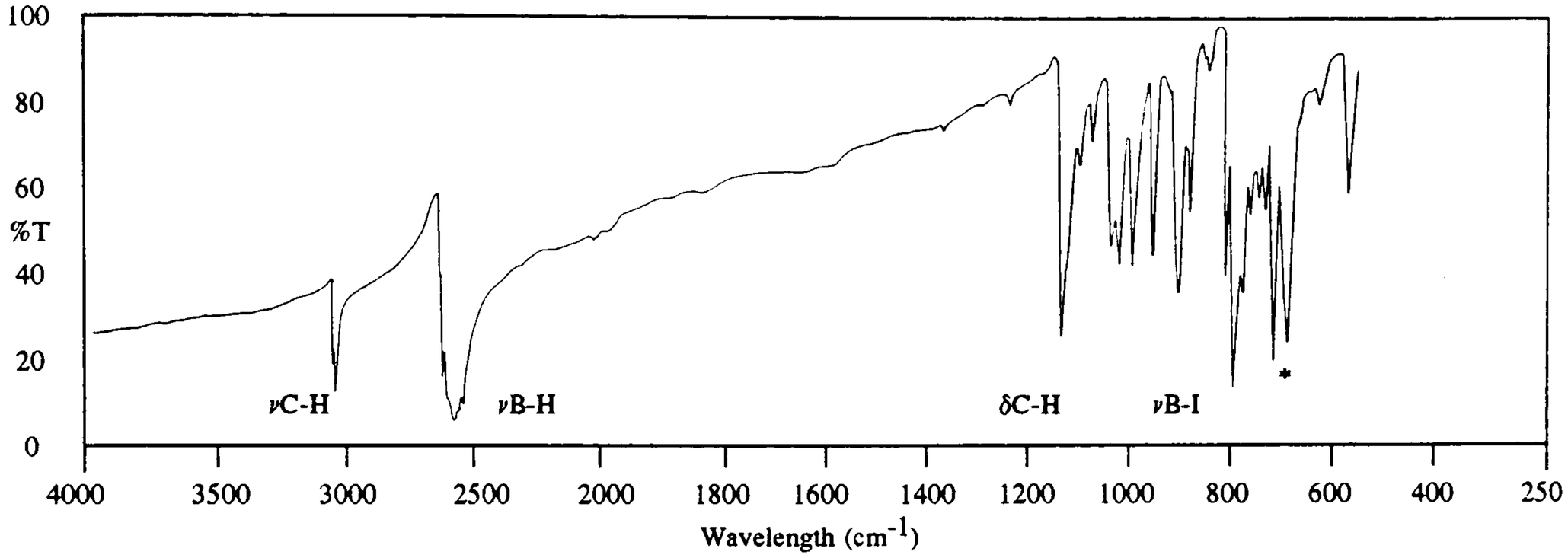
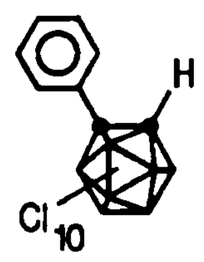
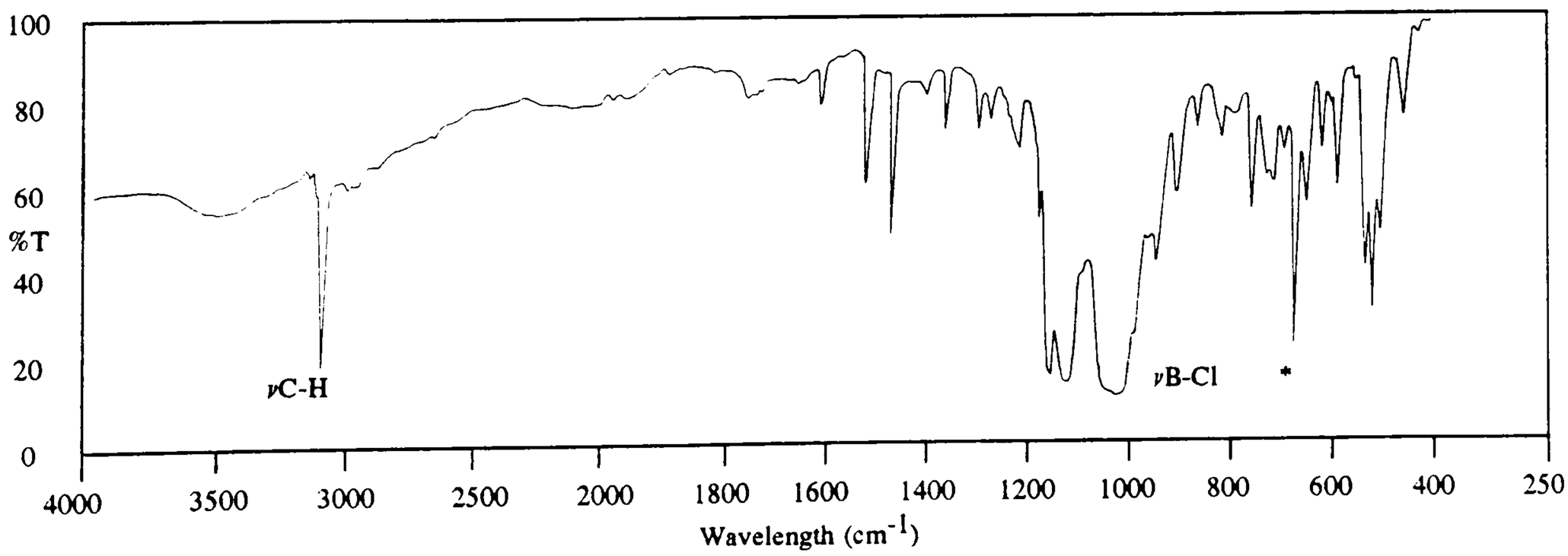
Infrared spectrum of 9-iodo-*meta*-carborane, m-$C_2B_{10}H_{11}I$ (KBr disc; cm^{-1})



Infrared spectrum of 1-phenyl-3,4,5,6,7,8,9,10,11,12-decachloro-*ortho*-carborane, o-$C_6H_5CB_{10}Cl_{10}CH$ (KBr disc; cm^{-1})





MASS SPECTROSCOPY

Mass spectroscopy is a very useful tool for detecting the molecular mass of a compound. There are several techniques in mass spectroscopy such as electron impact (E.I.), positive chemical ionization (C.I.+), negative chemical ionization (C.I.-), fast atom bombardment (F.A.B.), field ionization (F.I.), field desorption (F.D.), plasma desorption (P.D.) and gas chromatography (G.C.)[8a,9a].

Ortho-carborane is the sample used to observe the technique most suitable for carborane derivatives. Boron has two naturally occuring isotopes ^{10}B and ^{11}B with a relative ratio of between 1 : 3.77 and 1 : 4.42[10]. If the boron isotope ratio is 1 : 4 for ^{10}B : ^{11}B and only the molecular ion (M^+ or M^-) is present, the mass spectrum of *ortho*-carborane should show an isotope distribution between m/e 136 and 146 with base peak of m/e 144 (M^+ or M^-) corresponding to $^{12}C_2{}^1H_{12}{}^{10}B_2{}^{11}B_8$. Small peaks of m/e 147 and 148 are also present due to the carbon isotope, ^{13}C (1.1% natural abundance in carbon).

Electron impact is the most common technique in mass spectroscopy where the ions formed by an electron beam acting on the vaporized sample are recorded. The sample molecule (M) becomes a molecular ion ($M^{+\cdot}$) on electron impact[9a].

$$e + M \longrightarrow M^{+\cdot} + 2e$$

The molecular ion of less stable organic compounds usually disintegrates rapidly to a positively charged fragment (A) and a radical (B).

$$M^+ \longrightarrow A^+ + B^\cdot$$

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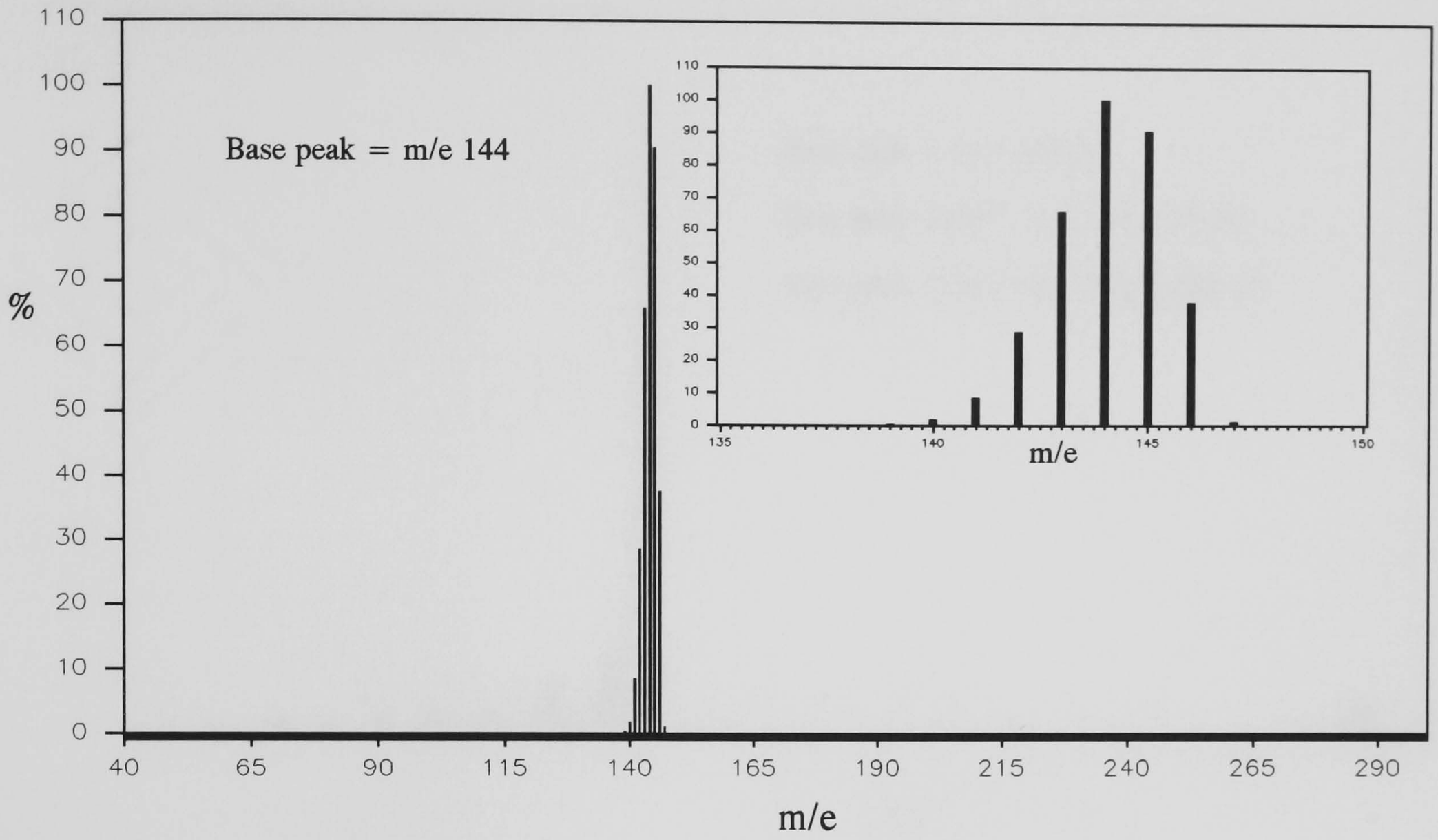
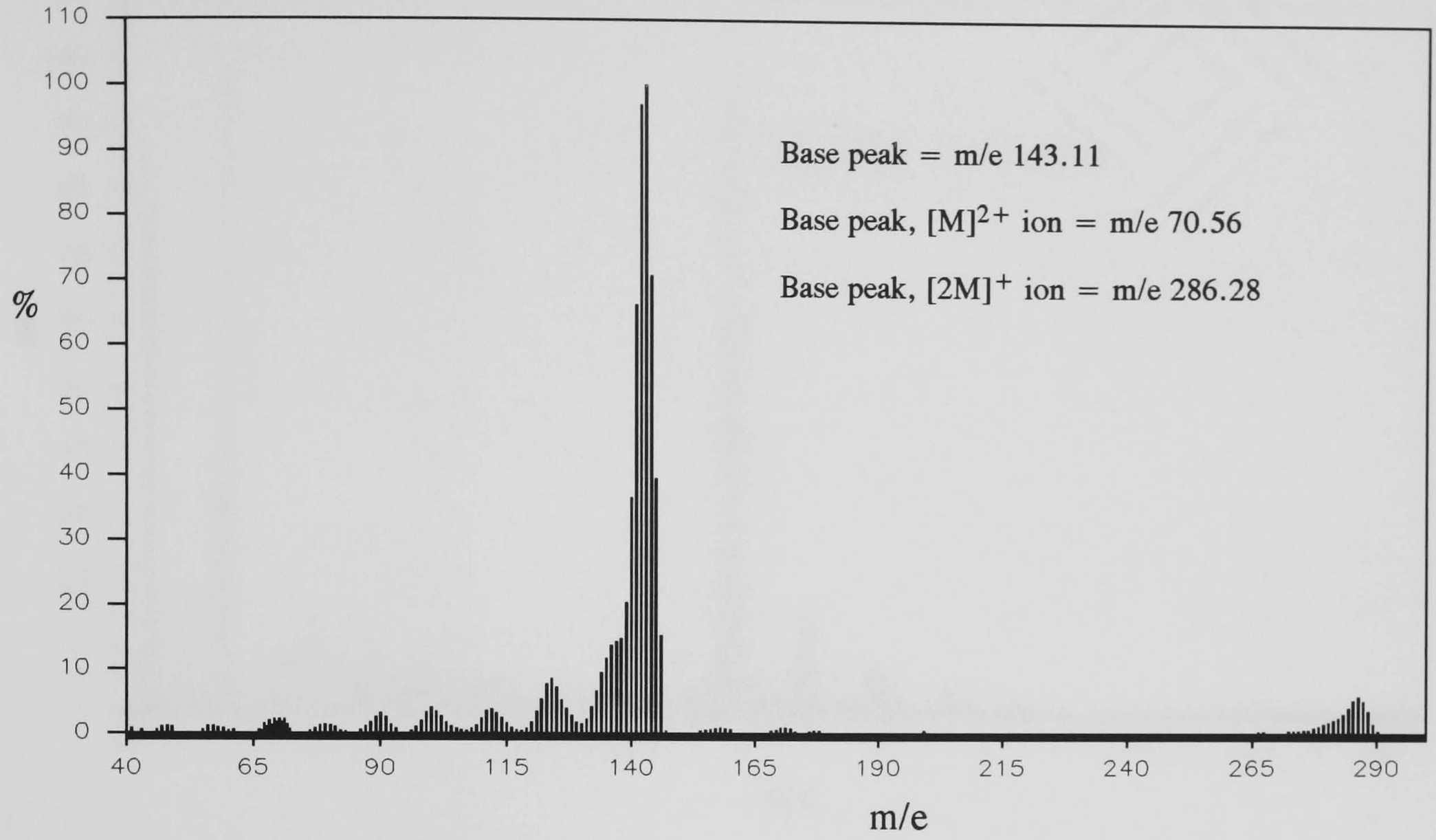
Theoretical mass spectrum of $1,2\text{-}C_2B_{10}H_{12}$



If the molecular ion remains intact long enough to reach the detector, a molecular ion peak is observed.

The E.I. mass spectrum of *ortho*-carborane (all mass spectra are produced using a VG Analytical Type 70-70E mass spectrometer with ionizing voltage at 70eV) showed a base peak of m/e 143 $[(M\text{-}1)^+]$ with an isotope distribution between m/e 130 and 146. Smaller groups of peaks with isotope distributions at m/e 41-131 were also observed. Two groups of peaks at m/e 266-290 and m/e 66.5-71.5 indicate dimer ions and doubly charged ions respectively.

Electron impact mass spectrum of $1,2\text{-}C_2B_{10}H_{12}$



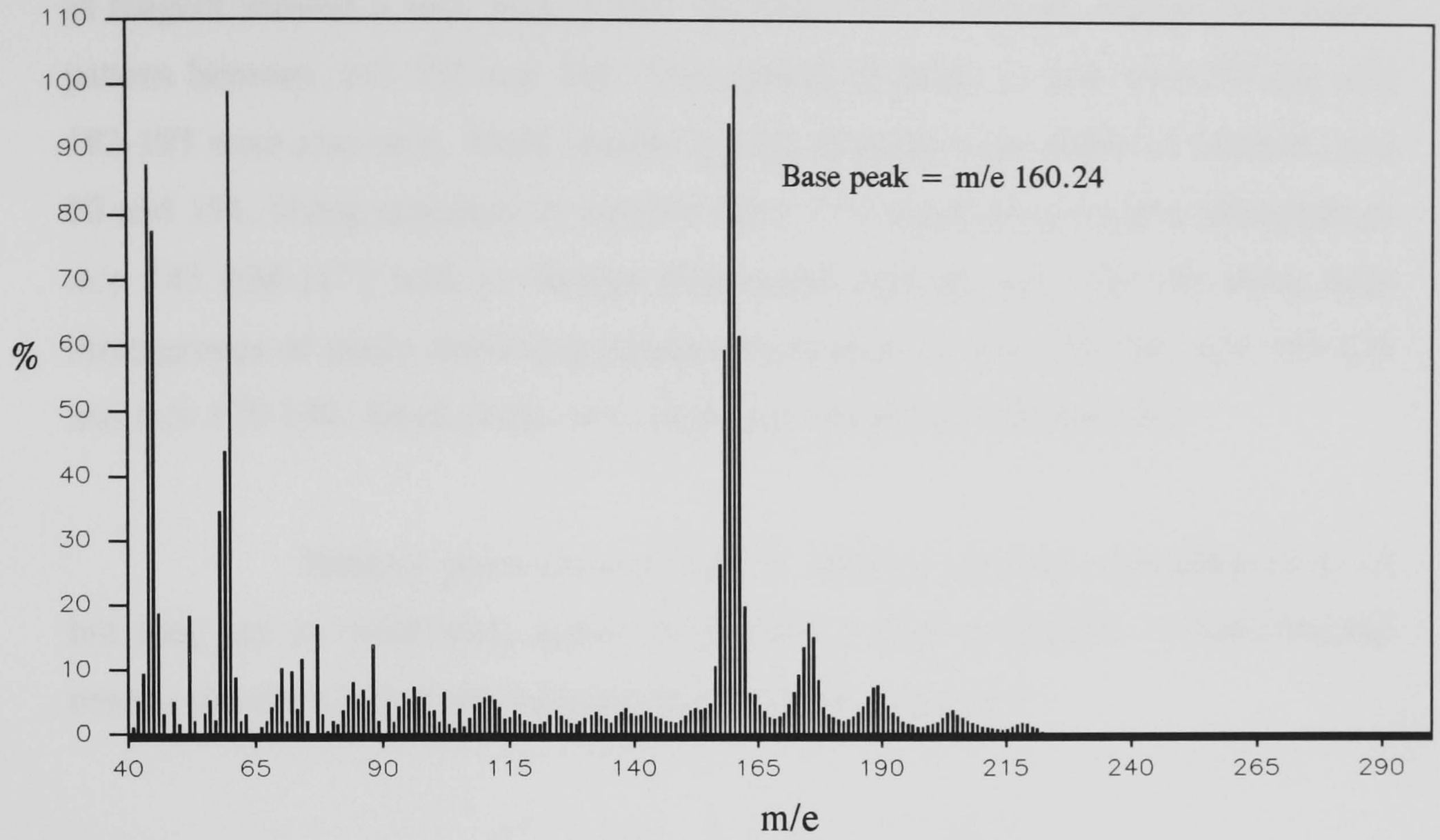
Positive chemical ionization (C.I.+) technique is like E.I. but with a reagent gas like ammonia present in excess over the sample. The reagent (R) is ionized by electron impact and reacts with neutral molecules to form secondary ions[9b].

$$R + e \longrightarrow R^{+\cdot} + 2e$$

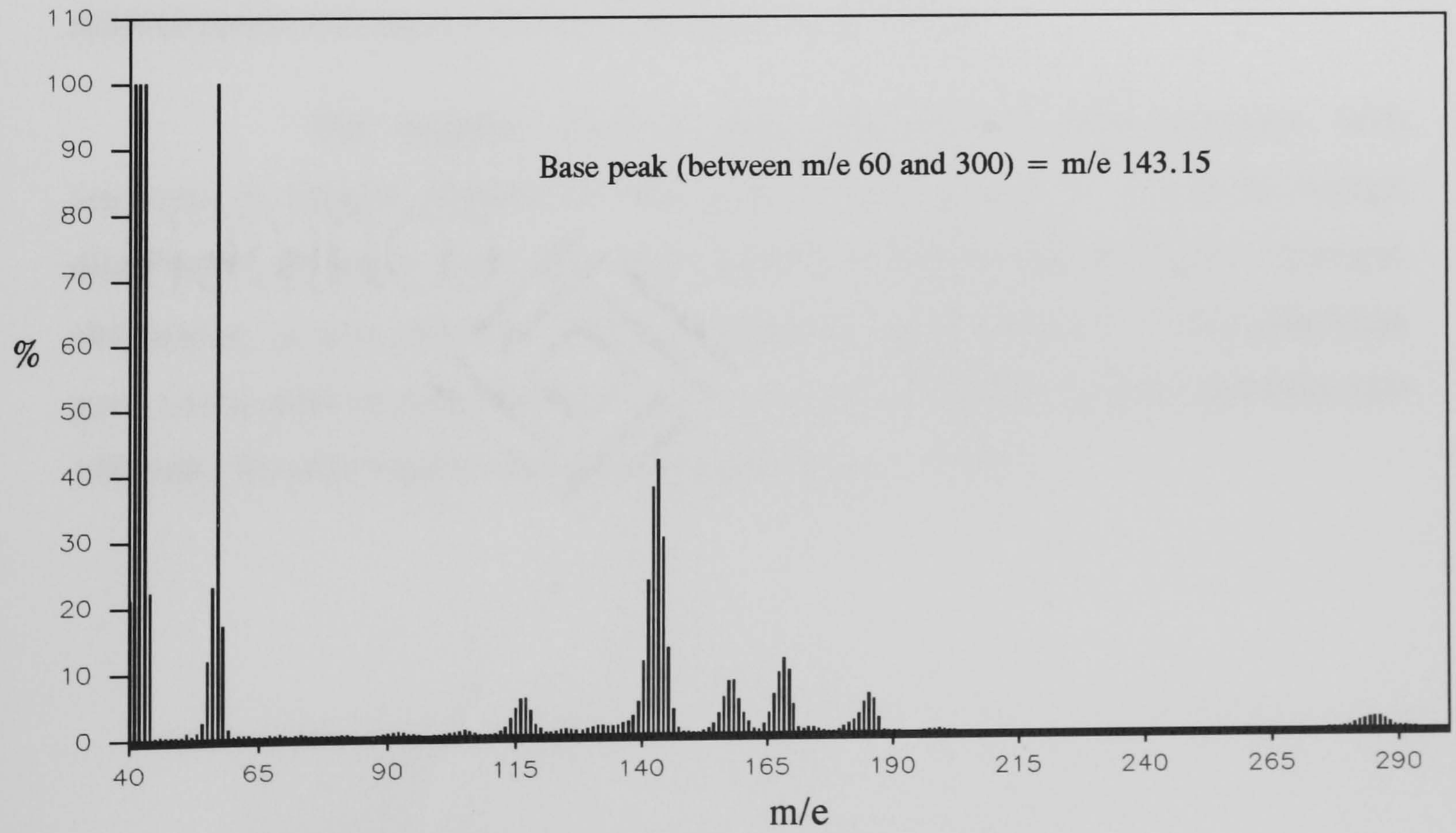
$$R^{+\cdot} + R \longrightarrow A^{+} + B^{\cdot}$$

The secondary ion (A^+) reacts with the sample molecule (M) to give a quasi-molecular ion $(M+C)^+$ in which C is usually a fragment of the reagent, commonly a proton. The quasi-molecular ion usually undergoes less fragmentation compared to the molecular ion (since it retains all its valence electrons) so the quasi-molecular ion peak is prominent with respect to the fragment peaks in a C.I.+ mass spectrum compared to E.I.

Positive chemical ionization spectrum of o-$C_2B_{10}H_{12}$ with ammonia



Positive chemical ionization spectrum of o-$C_2B_{10}H_{12}$ with isobutane



The C.I.+ mass spectrum of *ortho*-carborane formed with ammonia as reagent showed a base peak at m/e 160 $[(M+16)^+]$ with an isotope distribution pattern between m/e 155 and 165. Two groups of peaks at m/e 166-179 and m/e 183-193 were also seen. Much smaller groups of peaks were observed between m/e 80 and 154. Using isobutane as reagent, the C.I.+ spectrum showed a base peak of m/e 143 $[(M-1)^+]$ with an isotope distribution between m/e 130-146 along with three groups of peaks containing isotope distributions at m/e 150-164, m/e 165-174 and m/e 175-190. Small peaks were observed between m/e 60 and 129.

Reagent gases are also used in negative chemical ionization (C.I.−) but they act as moderating agents to produce a high population of near-thermal energy electrons which are captured by the sample molecules[8b].

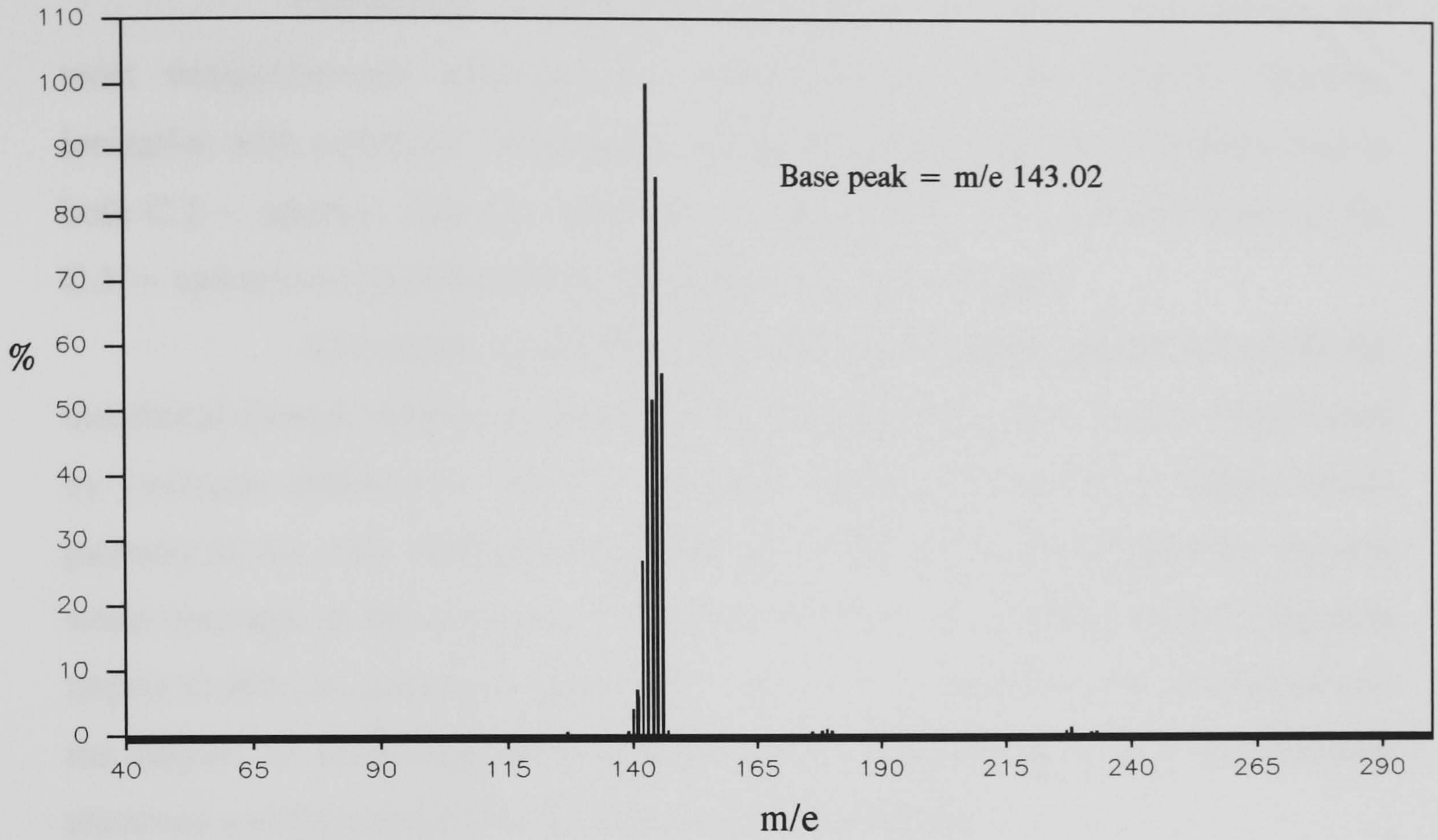
$$e^- + M \longrightarrow M^{-\cdot}$$

The essential properties for molecules to become long-lived negative molecular ions are high molecular symmetry, a large number of atoms, electron delocalization and dipole moment exceeding 1.625 debye[11].

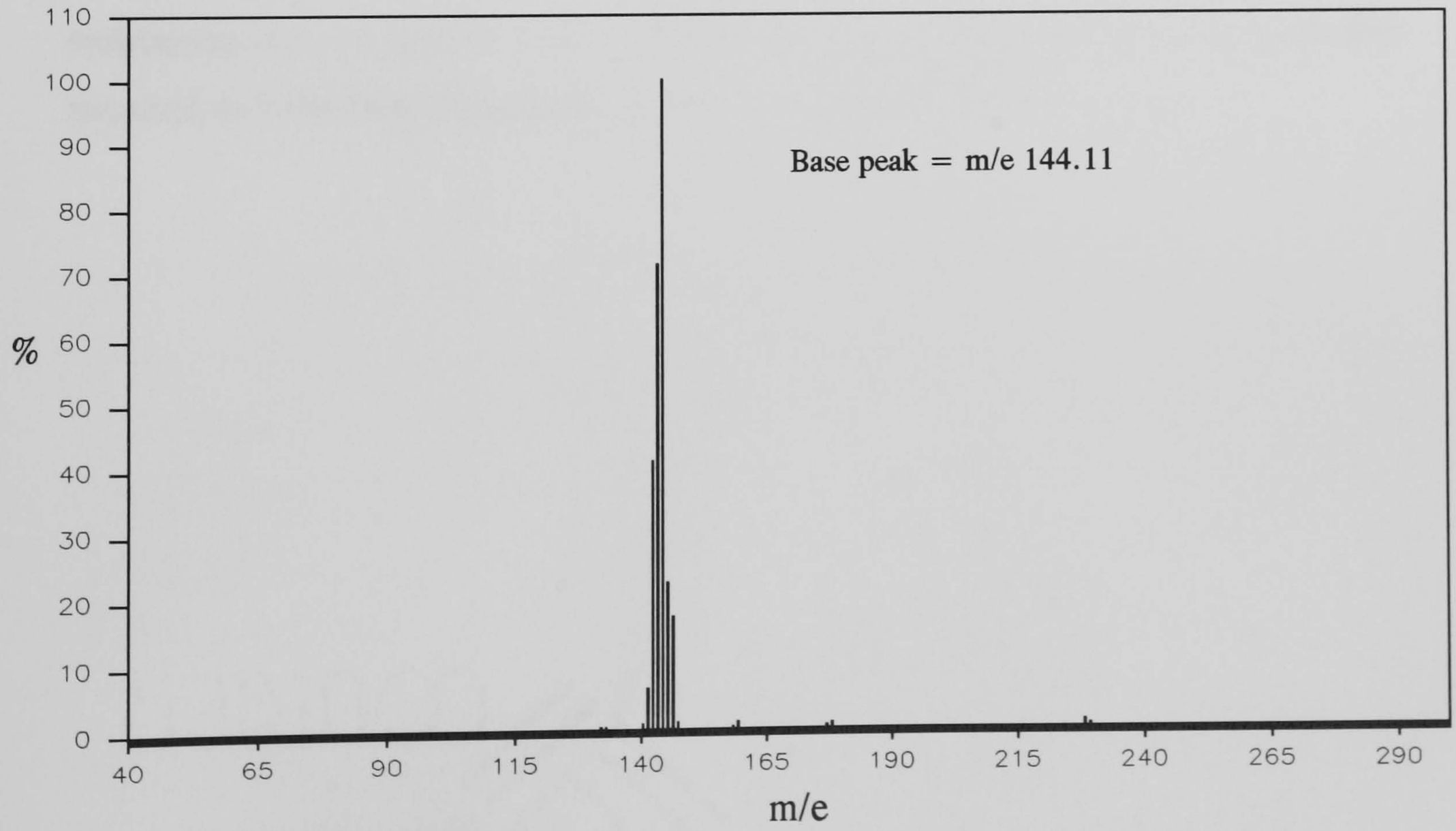
The negative (C.I.−) mass spectrum of *ortho*-carborane with ammonia as reagent showed the base peak at m/e 143 $[(M-1)^-]$ with an isotope distribution different from the other spectra, probably due to higher hydrogen abstraction, at m/e 138-146. Using isobutane as reagent, the C.I.− mass spectrum gave a base peak at m/e 144 (M^-) with an isotope distribution pattern between m/e 140-148. No other peaks were present in both C.I.− spectra.

11. Mazunov V.A. Nekrasov Yu.S. Khvostenko V.I. Stanko V.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1983 197-199

Negative chemical ionization spectrum of o-$C_2B_{10}H_{12}$ with ammonia



Negative chemical ionization spectrum of o-$C_2B_{10}H_{12}$ with isobutane



Comparing the calculated spectrum to all experimental spectra, the most straightforward technique for *ortho*-carborane is the negative chemical ionization with isobutane. There are no peaks formed by cage fragmentation seen in both C.I.− spectra. The E.I. technique is preferred to C.I.+ in this study as the C.I.+ spectra are complicated by the quasi-molecular ion peaks.

All isotope distribution patterns in experimental spectra do not fit the theoretical isotope distribution pattern well indicating that the picture is complicated by hydrogen abstraction. The E.I. spectrum showed that the main fragmentation pathway of the *ortho*-carborane molecular ion has to be the dehydrogenation process while cleavage of the carborane framework occurs to a negligible degree. Electron impact studies on carboranes have shown that up to 12 hydrogens are abstracted and the degree of dehydrogenation increases with increasing energy of the ionizing electrons and the temperature of the ionization chamber[10].

Although carborane E.I. and C.I.− mass spectra may not show the base peak as the correct molecular mass peak (M), the major characteristic carborane isotope distribution group of peaks usually contains it. Thus all carborane derivatives produced in this study have been characterized using E.I. or C.I.− techniques. E.I. is used as some carborane derivatives do not possess the properties required to form long-lived negative ions in negative C.I.[8c]

NUCLEAR MAGNETIC RESONANCE (N.M.R.) SPECTROSCOPY

A n.m.r. spectrum can be obtained from a compound if it contains an isotope with nuclear spin quantum number, I, > 0. The spin quantum number cannot be predicted in general but there are empirical rules[12]. Each nuclear isotope contains different numbers of protons (p) and neutrons (n). If p and n are even then I = 0 (no spin), p and n are odd then I = 1,2,3,... (integral spin) and p + n is odd then I = 1/2,3/2,5/2,... (half integral spin).

Isotopes with I = 1/2 have a uniform spherical charge distribution and with I > 1/2 the distribution is non spherical. The latter isotopes have an electric quadrupole moment which affects the relaxation time and coupling with neighbouring nuclei in n.m.r.[13a]

An *ortho*-carborane molecule has four suitable isotopes, ^{1}H (I = 1/2), ^{10}B (I = 3), ^{11}B (I = 3/2) and ^{13}C (I = 1/2) for n.m.r. spectroscopy so four types of one dimensional (1D) n.m.r. spectra of this compound are possible i.e. ^{1}H, ^{10}B, ^{11}B and ^{13}C.

The scale in a 1D n.m.r. spectrum is usually in dimensionless units known as parts per million, ppm. It is calculated as

$$\text{ppm} = \frac{\nu \times 10^{6}}{\nu_{o}}$$

where ν = peak frequency in Hertz (Hz) and ν_o = applied frequency in Hz[13b]. The peaks produced from a sample are measured in ppm relative to the reference peak. This difference in ppm is called chemical shift, δ, which depends on the environment of the particular nucleus in a molecule. Each peak present in n.m.r. spectra can in principle be assigned to each resonating nucleus of the molecule by comparing with known chemical shifts of the same isotope in a similar environment.

However if coupling of a nucleus of I = 1/2 with another of I = 1/2 occurs, its peak is split into two in its n.m.r. spectrum. The difference between the peaks as a result of coupling is known as a coupling constant, *J*, measured in Hz[13c].

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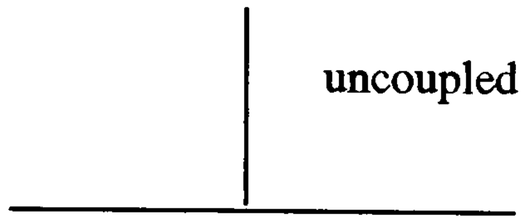
12. Banwell C.N. "Fundamentals of Molecular Spectroscopy" 3rd Edition McGraw-Hill London 1983 p243

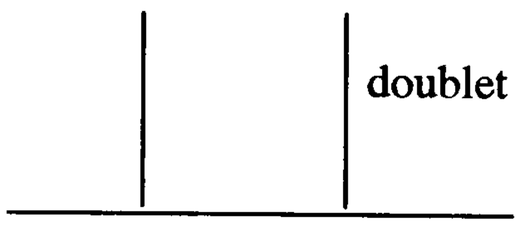
13. Silverstein R.M. Bassler G.C. Morrill T.C. "Spectroscopic Identification of Organic Compounds" 4th Edition John Wiley and Sons New York 1981 a) p181 b) p186 c) p190 d) p255 e) p249 f) p253 g) p257

The value of J depends on the type of isotopes, the distance between the isotopes and the environment of the isotopes. Homonuclear (same isotopes) and heteronuclear (different isotopes) couplings can help assign peaks in n.m.r. spectra but if the peak assignments are complicated by coupled peaks overlapping, then the complex spectrum can be simplified by removing the heteronuclear coupling peaks using a broad band noise decoupler[13d].

A. 

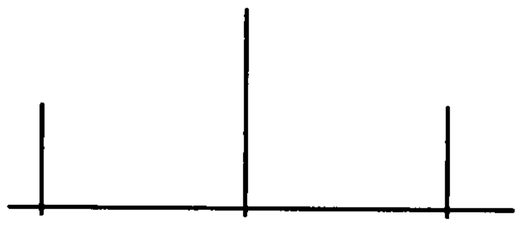
uncoupled peak of isotope A (I = 1/2)

frequency (Hz) or chemical shift (δ) axis

B. 

doublet peak by coupling with non-equivalent nucleus of the same isotope A′

distance between peaks = $J_{AA'}$

C. 

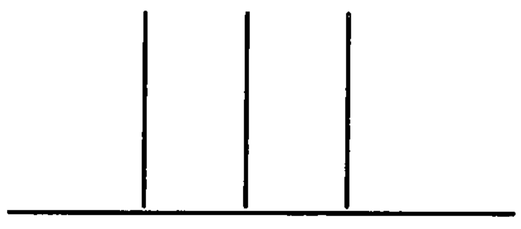
1:2:1 triplet peak by coupling with two other A′ nuclei

distance between peaks = $J_{AA'}$

D. 

doublet peak by coupling with different isotope B (I = 1/2)

distance between peaks = J_{AB}

E. 

1:1:1 triplet peak by coupling with different isotope C (I = 1)

distance between peaks = J_{AC}

D and E can become a singlet peak like A with a broad band noise decoupler.

Two dimensional (2D) nuclear magnetic resonance spectroscopy can aid in peak assignments if the peaks are difficult to assign in 1D n.m.r. due to lack of adequate information[14]. A 2D n.m.r. spectrum is produced from two time variables (one in 1D n.m.r.) and there are two classes of 2D n.m.r., J-resolved and correlated. J-resolved 2D n.m.r. has a coupling information axis and a chemical shift axis whereas correlated 2D n.m.r. spectroscopy (COSY) displays two chemical shift axes. 2D n.m.r. spectra can show which peaks are linked by homonuclear or heteronuclear coupling and thence they can often be assigned. Homonuclear 2D n.m.r. spectra are usually decoupled for simplicity.

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14. Benn R. Gunther H. *Angew. Chem. Int. Ed. Engl.* 1983 **22** 350-380

Proton Nuclear Magnetic Resonance Spectroscopy

250MHz ^1H n.m.r. spectra have been obtained for all derivatives described in this thesis that are soluble in common deuterated solvents. For proton n.m.r., the sample is dissolved in a solvent which needs to be free of protons to reveal a spectrum from the sample protons so deuterated solvents are used. The reference peak for ^1H n.m.r. is tetramethylsilane, Me_4Si, at 0.00ppm but $CHCl_3$, C_6D_5H and $CHD_2(CH_3)CO$ (present in small amounts in $CDCl_3$, C_6D_6 and $(CD_3)_2CO$) are used as references at 7.26, 7.15 and 2.05 ppm respectively in this study.

1D proton n.m.r. spectra of carborane derivatives in this study show characteristic peaks; the protons of carboranyl C-H give a broad singlet and carboranyl B-H give either several broad peaks or a single very broad peak with low intensity in the region of 4.5-0.5 ppm. Protons not directly bonded to the carborane cage give sharp, clean peaks except protons involved in hydrogen bonding and protons bonded to an isotope with $I > 1/2$ like nitrogen (^{14}N, $I = 1$) due to the quadrupole moment in the latter isotope.

The broad singlet of the carboranyl C-H is due to the electron-acceptor effect of the cage and positively charged cage carbon making the proton more acidic and thus solvent dependent as hydrogen-bonding interactions occur[15]. The hydrogen-bonding effect of the carboranyl C-H peak in 1-methyl-*ortho*-carborane is shown by its solvent sensitivity: it is observed at 4.75 ppm in pyridine and 3.43 ppm in carbon tetrachloride.

The carboranyl C-H peak is also affected by aromatic solvents e.g. benzene. It is shifted upfield in aromatic solvents compared to non-aromatic solvents and shifts are also observed to a smaller degree with carboranyl B-H peaks. The charges on the hydrogen atoms of the parent carboranes have been calculated from these shifts known as aromatic-solvent-induced-shifts (ASIS)[16,17].

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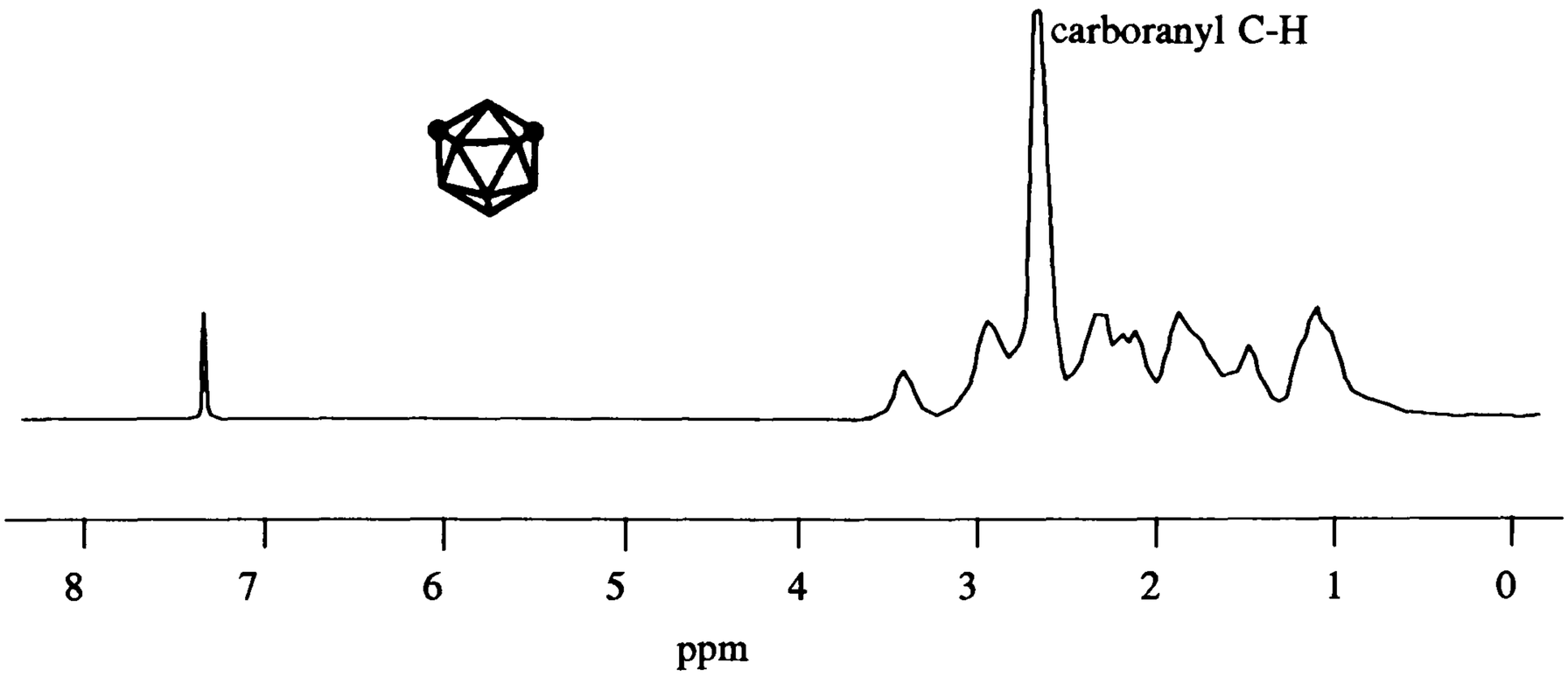
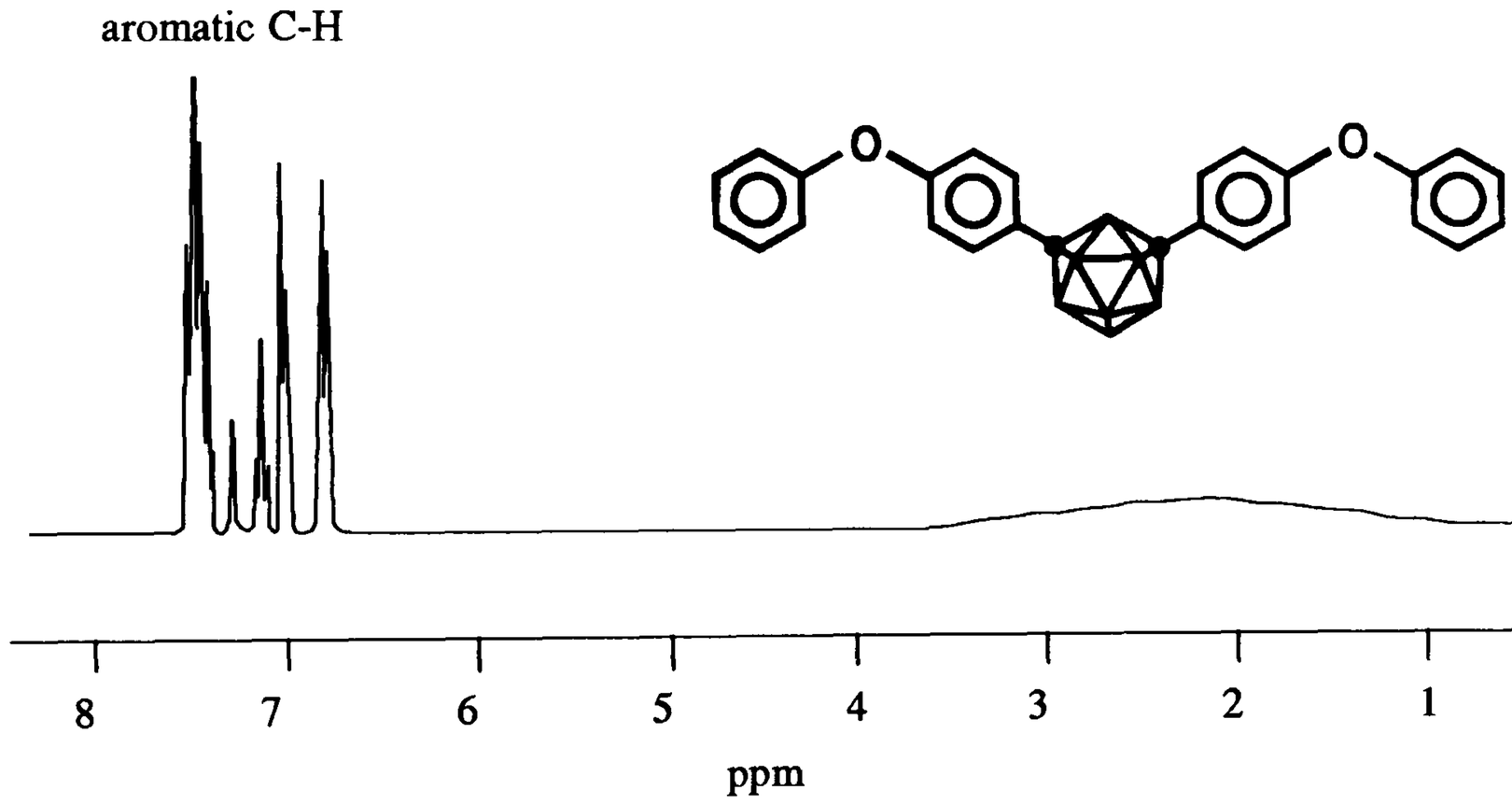
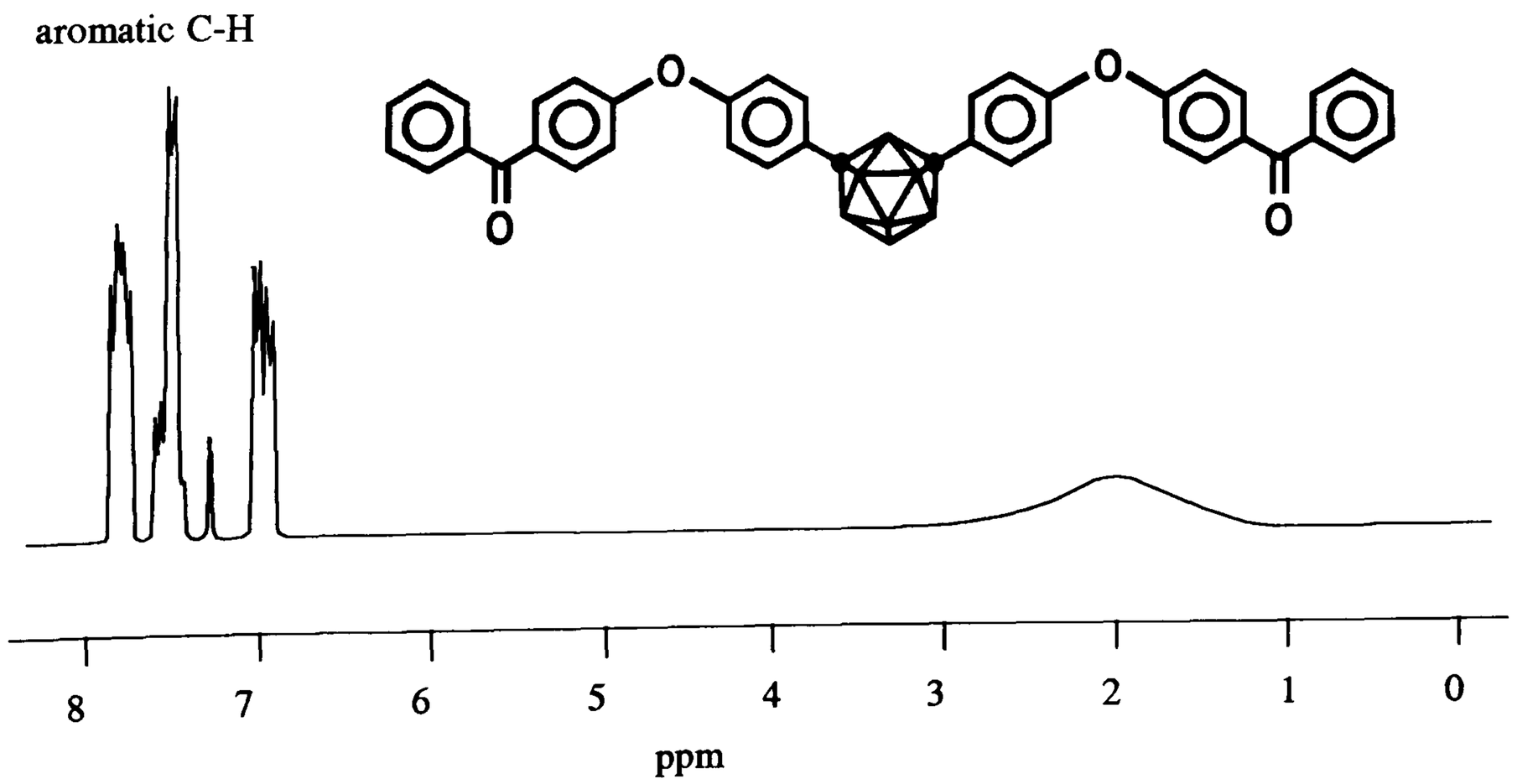
17. Jarvis W. Abdou Z.J. Onak T. *Polyhedron* 1983 **2** 1067-1070

^{1}H N.M.R. [250 MHz] solvent $CDCl_3$, referenced to 7.26ppm ($CHCl_3$).

The signals due to boron-attached protons lose their resolution as the size of the substituent groups increases.







The carboranyl B-H peaks are complex as each proton resonance is at least a quartet of very broad lines arising from $J_{^{11}B-^{1}H}$ coupling and scalar relaxation associated with ^{11}B (I=3/2) and ^{10}B (I=3) isotopes[18]. $J_{^{1}H-^{1}H}$ values are not seen as they are only about 15Hz[19]. Assignments of B-H peaks in ^{1}H n.m.r. of carborane derivatives on the basis of their $J_{^{11}B-^{1}H}$ values are almost impossible due to very broad and overlapping peaks.

The cage B-H peaks are found to be temperature dependent, the intensities of the B-H peaks in *meta-* carborane decrease to a very low broad peak at $-100°C$ then become a broad singlet at $-134°C$[20,21]. This is explained by boron quadrupole-induced $^{1}H-^{10}B,^{11}B$ spin decoupling. The quadrupole-induced decoupling effect increases with increasing molecular volume and ^{1}H n.m.r. spectra showed a broad singlet B-H peak for carborane polymers[22].

Using $\{^{11}B$ broad band noise$\}$ decoupling, the B-H peaks are sharper but peak assignments cannot be carried out as there are few literature values of these protons in carborane derivatives. B-H peak assignments of a carborane derivative can be done by $^{1}H-\{^{11}B\}$ selective decoupling which requires information from its ^{11}B n.m.r. spectrum[18,23].

Uncoupled two dimensional (2D) $^{1}H-^{11}B$ n.m.r. COSY spectroscopy is of little use for icosahedral carboranes as too many peaks complicate the spectrum[24] but heteronuclear decoupling on both frequency axes gives a $^{11}B-^{1}H$ chemical shift correlation map which can assign B-H proton peaks directly from known ^{11}B peak assignments (or ^{11}B peaks from assigned B-H proton peaks) and also shows clearly the relation between various boron and proton peaks[25].

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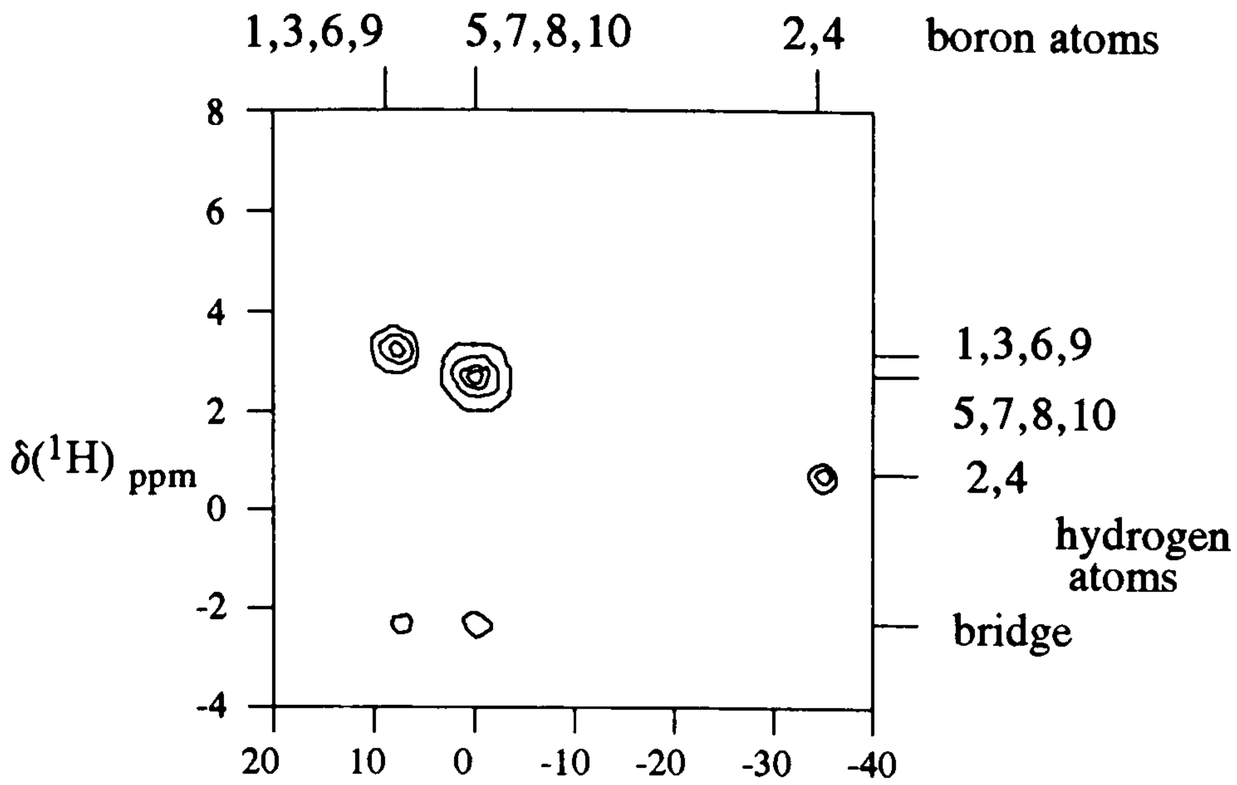

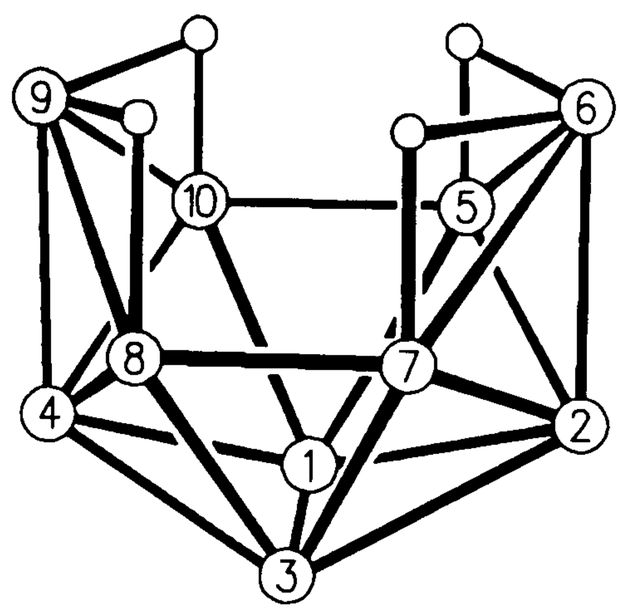

BH

H

Decoupled 2D ^{1}H-^{11}B COSY of *nido*-decaborane(14)[25]

2D homonuclear ^{1}H-^{1}H COSY with {^{11}B broad band noise} or selective {^{11}B} decoupling is a very powerful structural tool[19,26]. It could assign the B-H peaks of carborane derivatives without information from their ^{11}B n.m.r. spectrum. Much additional information can be obtained i.e. $^{3}J_{^{1}HBB^{1}H}$, $^{3}J_{^{1}HCB^{1}H}$, $^{3}J_{^{1}HCC^{1}H}$, ^{4}J and ^{5}J values.

As assignments of the B-H peaks were not essential in this study, the B-H peaks are defined as a broad multiplet between 4.0-1.0 ppm. However ^{1}H-^{1}H 2D COSY will be a very useful technique for studying the effect of temperature, substituents and solvents on the cage protons of carborane derivatives as the B-H peaks can be assigned without the need of other n.m.r. spectra for information.

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Boron-11 Nuclear Magnetic Resonance Spectroscopy

Boron has two naturally occurring isotopes ^{11}B (I=3/2) and ^{10}B (I=3) which are suitable for nuclear magnetic resonance spectroscopy. The ^{11}B isotope is preferred to ^{10}B in n.m.r. spectroscopy as the former has higher natural abundance, higher receptivity, relatively narrower signals and shorter relaxation times with respect to the latter[27]. However ^{10}B n.m.r. has been used in observing the thermal rearrangement of carboranes[28].

One-dimensional ^{11}B n.m.r. spectra of carboranes show broad peaks due in part to unresolved ^{11}B-^{11}B and ^{11}B-^{10}B couplings ($J_{^{11}B\text{-}^{11}B} < 20$Hz), quadrupole relaxation and partially collapsed multiplets[29]. The line widths can be narrowed in some cases by deleting the multiplication of the signal used to increase the ratio of signal to noise at the expense of an artificially broadened line[30].

The ^{11}B-^{1}H coupling constant, $J_{^{11}B\text{-}^{1}H}$, is found to vary between 148 and 188 Hz in carboranes[31]. $J_{^{11}B\text{-}^{1}H}$ values correlate well with the calculated value of s-orbital electron population present in the boron atom[32] and structural characteristics of the B-H bond where the major parameters are the cage "umbrella" angle and the number of adjacent cage carbon atoms[17]. The $J_{^{11}B\text{-}^{1}H}$ values are of the same order of magnitude as ^{11}B chemical shifts of icosahedral carborane derivatives giving ^{11}B n.m.r. spectra of overlapping peaks which makes peak assignments difficult[33,34]. Partially relaxed Fourier transform (PRFT) n.m.r. can help peak assignments only if there is appreciable variation of spin-lattice relaxation times between the different ^{11}B isotopes[18,35]. Heteronuclear decoupling by {^{1}H broad band noise} reduces the doublets to singlets in ^{11}B n.m.r. spectra which aids peak assignments and chemical shift measurements[33].

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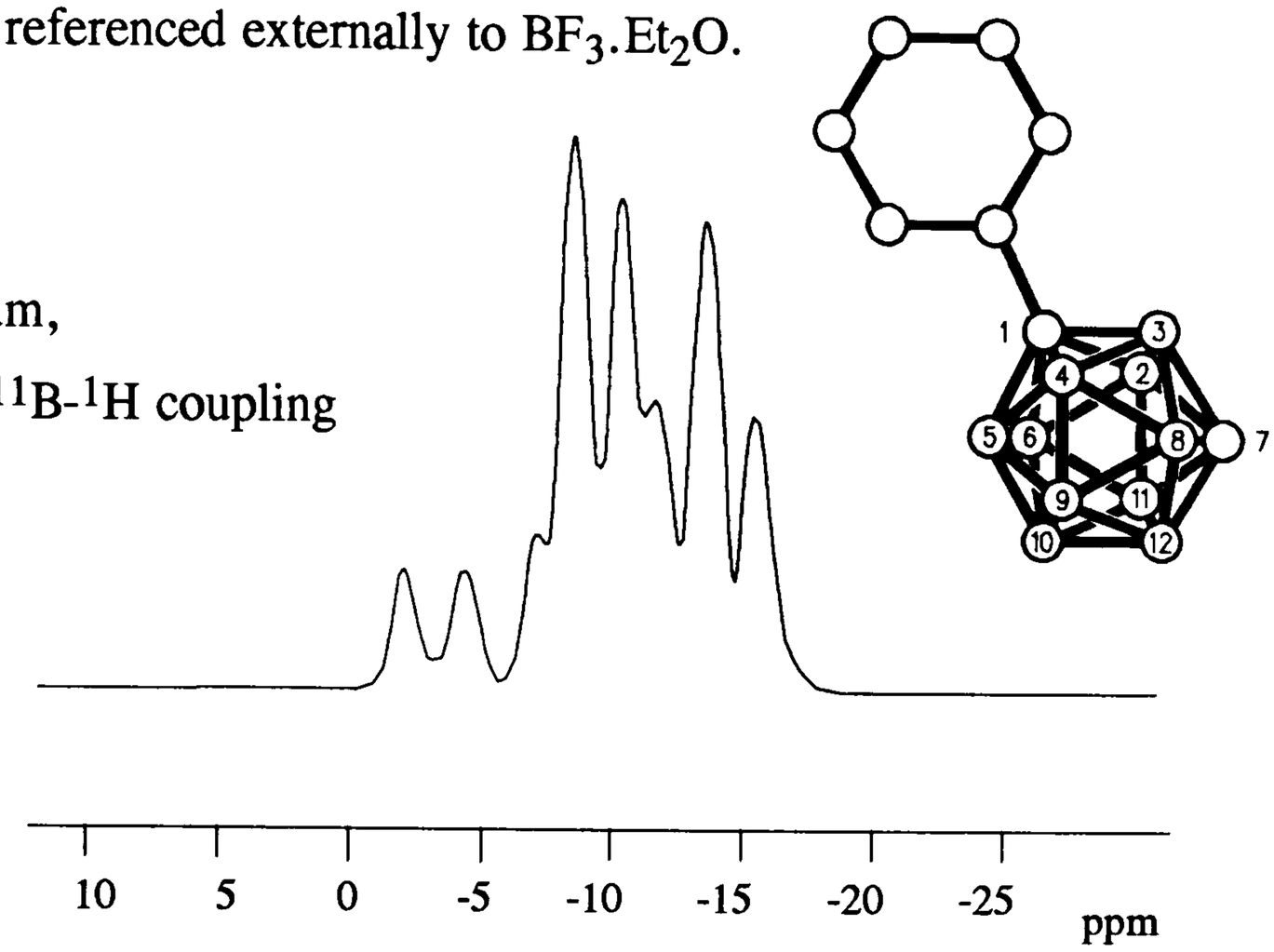
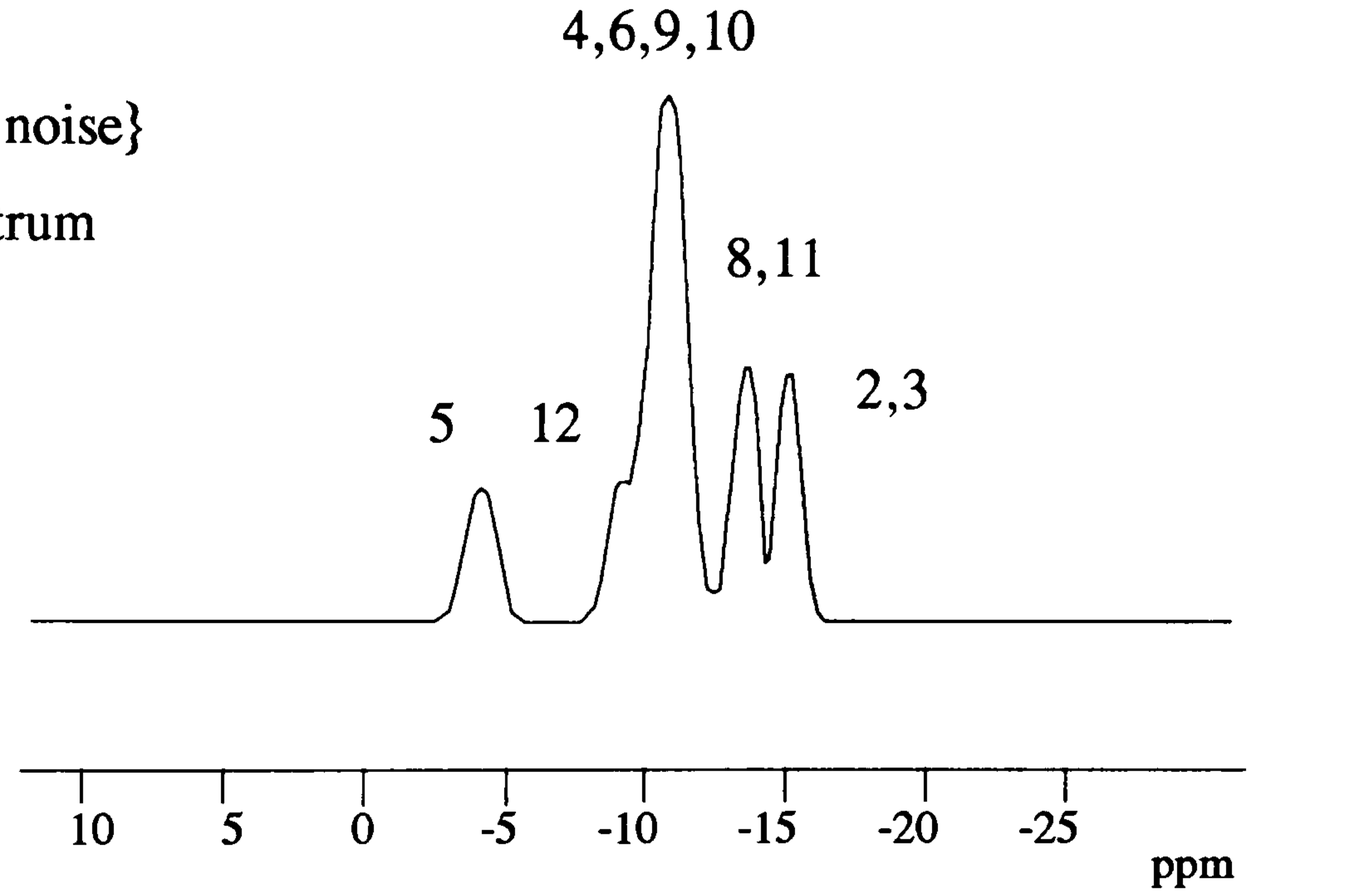
^{11}B N.M.R. [115MHz] of 1-phenyl-*meta*-carborane, solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$.

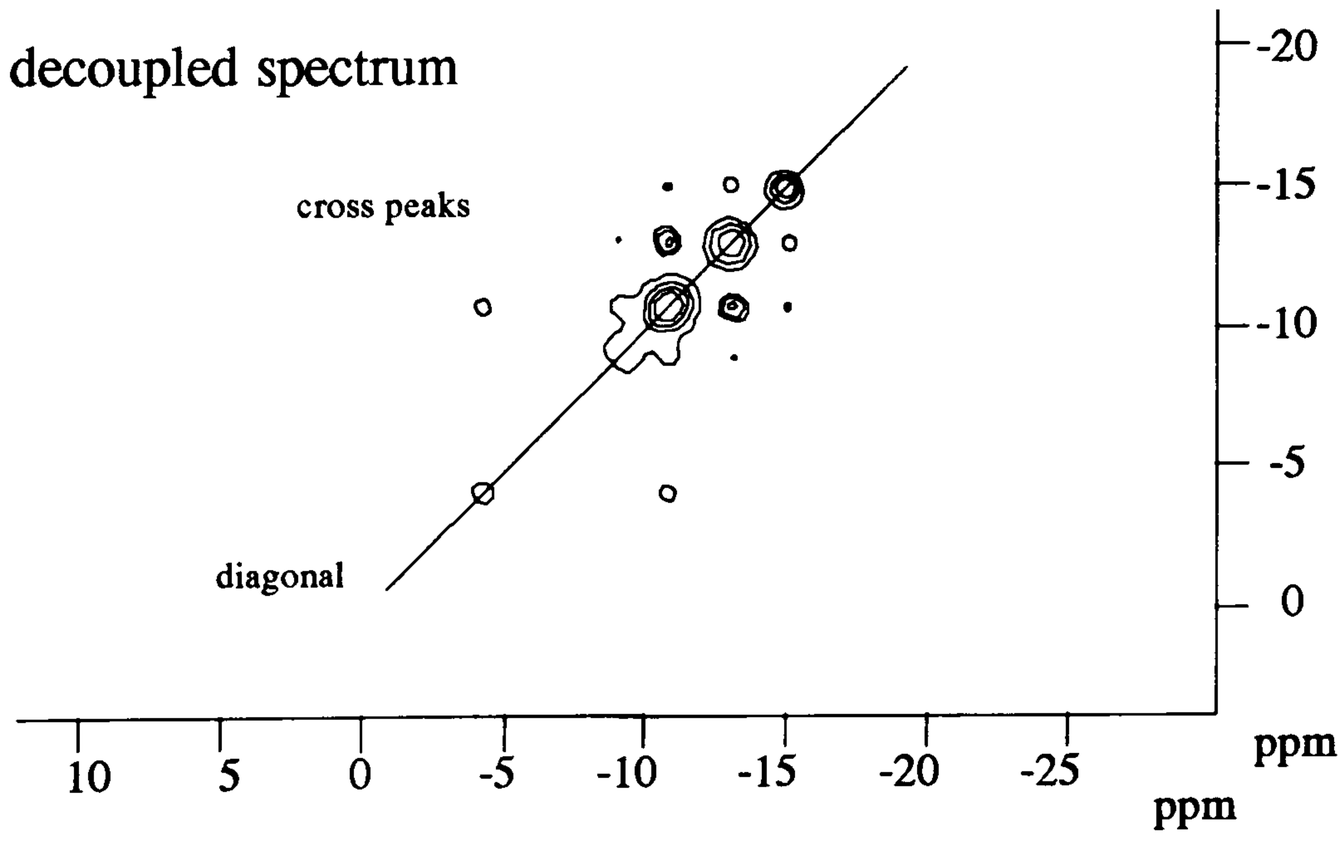


Coupled spectrum,
doublets from ^{11}B-^{1}H coupling

{^{1}H broad band noise}
decoupled spectrum



2D COSY {^{1}H} decoupled spectrum



^{11}B n.m.r. peaks can be assigned in carboranes using the ^{11}B-^{11}B double resonance technique which uses a second radio frequency field sweep to monitor the intensity of an isotope peak[36,37,38]. A ^{11}B-^{11}B double resonance spectrum is required for each non-equivalent atom and shows peaks formed by ^{11}B-^{11}B coupling between the resonating ^{11}B isotope and ^{11}B isotopes bonded to it.

Decoupled 2D ^{11}B-^{11}B COSY spectroscopy is an excellent technique for assignment of ^{11}B n.m.r. peaks in carboranes as it shows which ^{11}B peaks couple and so by implication which boron atoms are directly connected, as in ^{11}B-^{11}B double resonance technique, but all peaks from ^{11}B-^{11}B couplings are shown on one spectrum[23,26,39,40,41]. However there are some limitations, 'expected' coupling peaks are sometimes missing and coincidential overlap of ^{11}B peaks gives ambiguous information[19].

^{11}B chemical shifts are dominated by paramagnetic shielding[42]. Calculated boron electron densities[32] and geometrical rules[43] have been found to correlate well with known ^{11}B chemical shifts. The simple geometrical rules contain antipodal (AE), butterfly (BE) and neighbour (NE) effects on ^{11}B chemical shifts of carboranes. The effects on the shift decrease in order AE > BE > NE.

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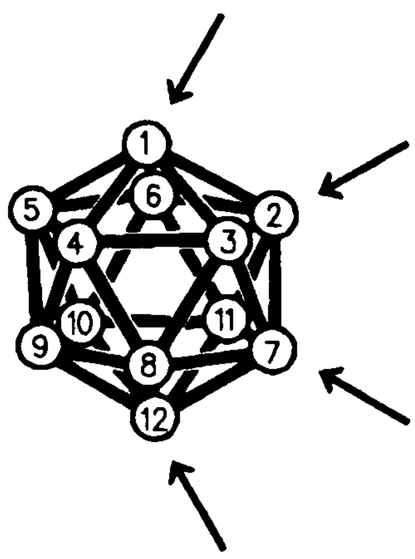
Geometrical rules for cage ^{11}B n.m.r. chemical shifts[43].

If atom 1 or its environment changes, the effect on the ^{11}B chemical shift of a cage boron atom depends on its geometric position.

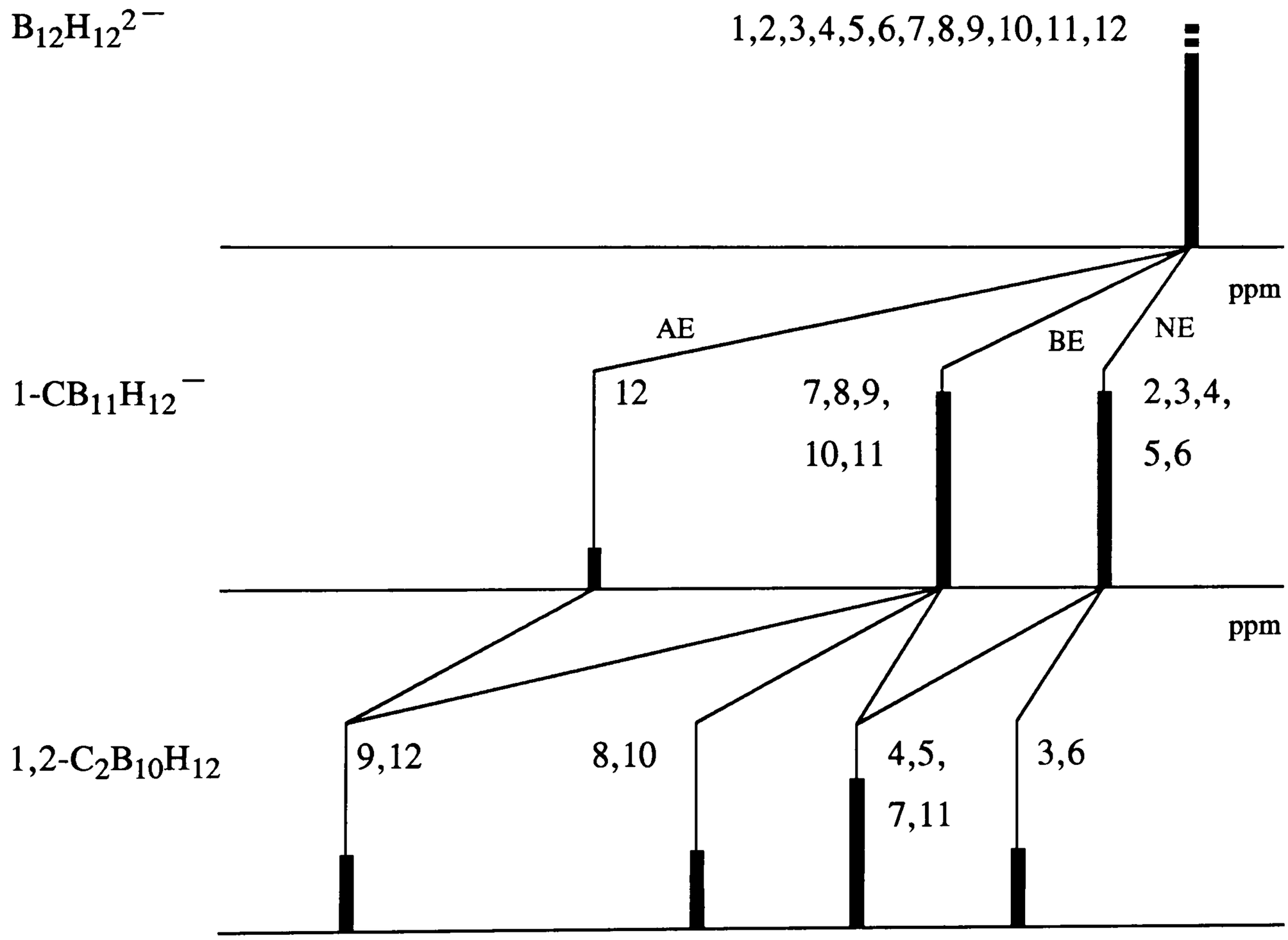


Neighbour Effect (NE) on atoms directly bonded to 1

Butterfly Effect (BE) on atoms not directly bonded or opposite to 1

Antipodal Effect (AE) on atom directly opposite 1

Theoretical ^{11}B chemical shifts of 1,2-$C_2B_{10}H_{12}$



Experimental ^{11}B chemical shifts of 1,2-$C_2B_{10}H_{12}$

δ_{ppm}	intensity	position of boron
-3.80	2	9,12
-10.60	2	8,10
-15.00	4	4,5,7,11
-16.07	2	3,6

The antipodal effect is present in all ^{1}H, ^{11}B and ^{13}C n.m.r. chemical shifts of icosahedral carborane derivatives[15,44,45,46,47,48,49,50,51]. In substituted carboranes, it was found to be similar to the positive mesomeric effect in substituted benzenes; an increase in electron density in the substituted atom leads to an increase in electron density in the opposite atom[52]. The negative mesomeric effects (i.e. decrease in electron density) observed in aromatic compounds are different from the antipodal effects in carboranes as there is negligible electron donation from an electron-deficient carborane skeleton as opposed to an aromatic ring. However 1-halogeno-12-mercapto-*ortho*-carboranes did not show the expected antipodal effect based on the positive mesomeric effect[27].

It was proposed that a change in the chemical shift of an ^{11}B nucleus is proportional to the change in the electron density in *p*-orbitals while the electronegativity of the substituent is proportional to the electron density in the radially outward *sp* hybrid explains the antipodal effect[27]. Photoelectron spectral studies showed conjugative interaction between 'lone-pair' halogen *p*-orbitals and empty *p*-orbitals of the cage[53]. For simplicity the octahedral cage molecule i.e. $C_2B_4H_5X$ is used as an example overleaf. Both surface *p*-orbitals in the antipodal cage atom are expected to participate in the conjugative interaction of surface *p*-orbitals compared to participation of one surface *p*-orbital in other unsubstituted cage atoms which could explain the antipodal effect on cage atoms in carboranes[54,55].

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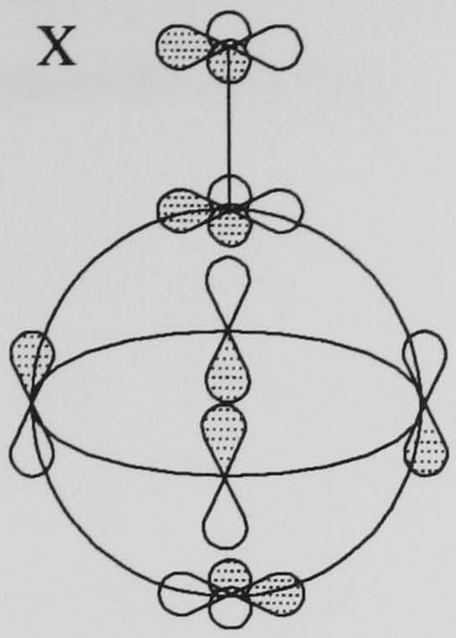


Surface p-orbitals of $C_2B_4H_5X$ (X = substituent)

Proposed antipodal effect mechanism[27]

Electrons from two *p*-orbitals of non-cage atom are passed to the empty surface *p*-orbitals of the cage where both *p*-orbitals of the substituted and antipodal cage atoms always participate whereas only one of the *p*-orbitals in other cage atoms take part in the conjugative interaction.

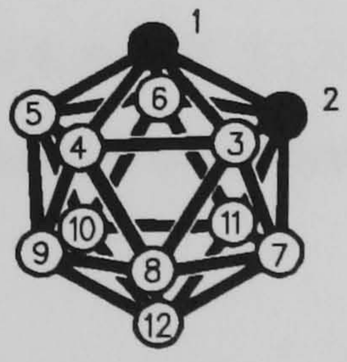
In this study decoupled 1D ^{11}B n.m.r. spectroscopy was used on a Bruker AC250 spectrometer with applied frequency 80MHz for all carborane derivatives produced that are soluble. The reference compound, boron trifluoride etherate ($BF_3.Et_2O$), was used externally for all ^{11}B spectra at 0.00ppm. Decoupled 2D ^{11}B-^{11}B COSY was used to aid peak assignments of 1D spectra in carborane derivatives.

The tables below show the expected cross peaks in 2D ^{11}B-^{11}B COSY spectra of various carborane derivatives.

Ortho-carborane derivatives.

A. If 3 ≡ 6, 4 ≡ 5 ≡ 7 ≡ 11, 8 ≡ 10, 9 ≡ 12

e.g. *ortho*-carborane



	3,6	4,5, 7,11	8,10	9,12	Int.
3,6		●	●		2
4,5,7,11	●		●	●	4
8,10	●	●		●	2
9,12		●	●		2

4,5,7,11 and 8,10 peaks are unique.

3 ≡ 6 means the boron atom at position 3 is identical to the boron at 6 but different to other boron atoms (i.e. 4,5,7,8,9,10,11,12 positions) in the cage. A dot indicates a cross peak that should be observed in the 2D ^{11}B n.m.r. spectrum between the two 1D ^{11}B n.m.r. peaks. Int. = intensity of 1D ^{11}B n.m.r. peak.

B. If 3 ≡ 6, 4 ≡ 5, 7 ≡ 11, 8 ≡ 10

e.g. 9-iodo-*ortho*-carborane

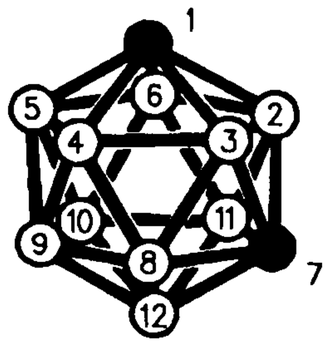
	3,6	4,5	7,11	8,10	9	12	Int.
3,6		●	●	●			2
4,5	●			●	●		2
7,11	●			●		●	2
8,10	●	●	●		●	●	2
9		●		●		●	1
12			●	●	●		1

8,10 peak is unique

Meta-carborane derivatives

C. If 2 ≡ 3, 4 ≡ 6 ≡ 8 ≡ 11, 5 ≡ 12, 9 ≡ 10

e.g. *meta*-carborane



	2,3	4,6, 8,11	5,12	9,10	Int.
2,3		●			2
4,6,8,11	●		●	●	4
5,12		●		●	2
9,10		●	●		2

Unique peaks are 2,3 and 4,6,8,11

D. If 2 ≡ 3, 4 ≡ 6, 8 ≡ 11, 9 ≡ 10

e.g. 1-phenyl-*meta*-carborane

	2,3	4,6	8,11	5	12	9,10	Int.
2,3		●	●				2
4,6	●		●	●		●	2
8,11	●	●			●	●	2
5		●				●	1
12			●			●	1
9,10		●	●	●	●		2

2,3 peak is unique

E. If 4 ≡ 8, 6 ≡ 11, 5 ≡ 12

e.g. 9-iodo-*meta*-carborane

	2	3	4,8	6,11	5,12	9	10	Int.
2		●		●				1
3	●		●					1
4,8		●			●	●		2
6,11	●				●		●	2
5,12			●	●		●	●	2
9			●		●		●	1
10				●	●	●		1

5,12 peak is unique

Carbon-13 Nuclear Magnetic Resonance Spectroscopy

Carbon has two naturally occurring isotopes, ^{12}C (I=0) and ^{13}C (I=1/2) where only the latter isotope has properties suitable for n.m.r. spectroscopy[13e]. The ^{13}C isotope however is low in natural abundance (1.1% in carbon) and very low in sensitivity compared to ^{1}H and ^{11}B isotopes. The ^{13}C n.m.r. spectrum is best seen as {^{1}H broad band noise} decoupled as ^{13}C-^{1}H, ^{13}C-C-^{1}H and ^{13}C-C-C-^{1}H couplings complicate the spectrum. A single ^{13}C peak is observed from a particular ^{13}C nucleus in a molecule except when bonded to other non-proton isotopes containing $I > 0$. ^{13}C-^{13}C couplings are not usually seen due to low natural abundance of ^{13}C. Unlike in ^{1}H and ^{11}B n.m.r. spectra, the peak intensities do not correspond to the number of nuclei in the same chemical environment; they depend on relaxation time and consequently on the number of protons attached to the carbon[13f]. A ^{13}C nucleus with no proton directly attached gives a low intensity peak in the ^{13}C n.m.r. spectrum compared to ^{13}C nuclei with protons as the dipole-dipole interaction between ^{13}C and ^{1}H reduces the relaxation time so that the ^{13}C peak intensity increases.

Deuterated solvents e.g. $CDCl_3$ are used in ^{13}C n.m.r. as their ^{13}C peaks are reduced in intensity with respect to their proton analogues and in this case split into a 1:1:1 triplet arising from ^{2}D-^{13}C coupling[13g]. If a deuterated solvent peak overlaps a sample peak, the spin echo Fourier transform (SEFT) technique is probably best used to observe the sample peak as it selectively eliminates the deuterated peaks from the ^{13}C n.m.r. spectrum[3]. Tetramethylsilane is generally used as the reference peak at 0.00ppm in ^{13}C n.m.r. spectroscopy and the usual range of a proton decoupled ^{13}C n.m.r. spectrum is between 200-0ppm. There are many other 1D ^{13}C n.m.r. techniques like INEPT[56], DEPT, INADEQUATE, DANTE and 2D ^{13}C n.m.r. techniques, J-resolved and correlated, but they are of little use for ^{13}C n.m.r. assignments of carborane derivatives.

The icosahedral carborane framework contains two carbon atoms so proton decoupled 1D ^{13}C n.m.r. spectroscopy has been carried out in all carborane

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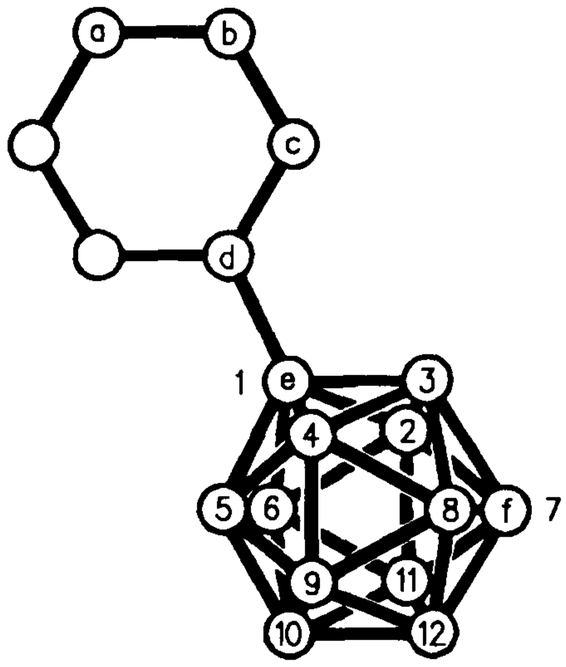
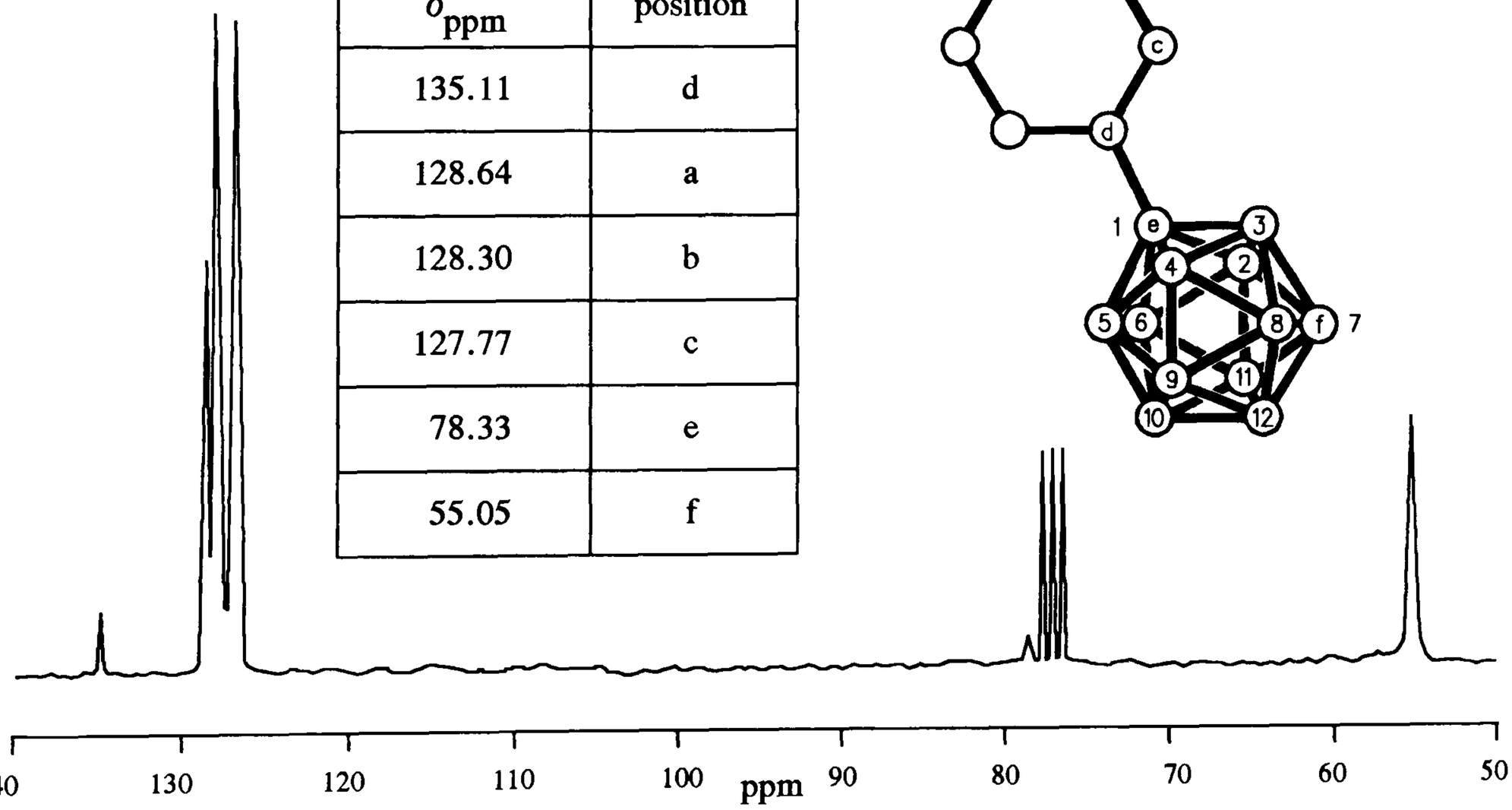
56. INEPT = insensitive nuclei enhanced by polarization transfer, DEPT = distortionless enchancement by polarization transfer, INADEQUATE = incredible natural abundance double quantum transfer experiment, DANTE = delays alternating with nutation for tailored excitation; Benn R. Gunther H. *Angew. Chem. Int. Ed. Engl.* 1983 **22** 350-380

derivatives in this study, which were soluble in suitable solvents, using a Bruker AC250 spectrometer with applied frequency of 60 MHz. The deuterated solvents used were $CDCl_3$, $(CD_3)_2CO$ and $(CD_3)_2SO$ referenced repectively as 77.0, 28.0 and 39.0ppm. Due to solvent effects on carboranyl ^{13}C peaks[48,57], $CDCl_3$ is used as standard solvent for most ^{13}C n.m.r. spectra produced in this thesis. If the solvent peak overlaps a sample peak, the solution is concentrated or a different deuterated solvent is used to observe the hidden peak. The peaks of non-cage ^{13}C nuclei bonded to cage boron atoms are not usually seen due to ^{11}B,^{10}B-^{13}C couplings[58]. These couplings could be eliminated by ^{11}B broad band or selective noise decoupling to give clear single ^{13}C peaks[59]. However the ^{13}C peak assignments of cage B - non-cage C in certain carborane derivatives are not essential in this thesis and thus are omitted in the experimental sections.

^{13}C N.M.R. 60MHz, {^1H broad band noise} decoupled, of 1-phenyl-*meta*-carborane, solvent $CDCl_3$ referenced at 77.0ppm.

δ_{ppm}	position
135.11	d
128.64	a
128.30	b
127.77	c
78.33	e
55.05	f





57. Fedin E.I. Antonovich V.A. Rhys E.G. Kalinin V.N. Zakharkin L.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1975 723-726

58. Zakharkin L.I. Kalinin V.N. Rhys E.G. Antonovich V.A. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1980 1446-1449

59. Koster R. Seidel G. Wrackmeyer B. *Angew. Chem. Int. Ed. Engl.* 1984 96 520-521

^{13}C n.m.r. spectroscopy is a very useful tool for carborane derivatives as it examines the antipodal effect[48,49] and electron delocalization[59,60,61] of the carborane cage by carboranyl ^{13}C peak values which are usually between 90 and 40 ppm. It is also important for structural determination of carborane derivatives containing many aromatic rings. Unlike ^{11}B n.m.r. spectroscopy the peak assignments are easy as only one or two carboranyl carbon peaks are possible, the ^{13}C n.m.r. peak values of organic substituents are known and coincidential overlap of peaks is rare. The ^{13}C n.m.r. peaks of compounds containing many aromatic rings are assigned with the help of ^{13}C n.m.r. spectra of similar compounds carried out in this study or found in literature[62,63] or both. For example the ^{13}C n.m.r. peak assignments of 1,2-bis(4-phenoxyphenyl)-*ortho*-carborane were determined by comparing with the ^{13}C n.m.r. spectra of diphenyl ether, 4,4′-phenoxybiphenyl and 4-iododiphenyl ether.

Fluorine-19 Nuclear Magnetic Resonance Spectroscopy

Fluorine has only one naturally occuring isotope ^{19}F (I = 1/2) which has excellent properties (surpassed only by ^{1}H isotope) for n.m.r. spectroscopy. The compound $CFCl_3$ was used as external reference at 0.00ppm and all ^{19}F spectra of fluorine-containing derivatives produced in this study were obtained from a Bruker AC250 spectrometer with an applied frequency of 235MHz.

60. Stanko V.I. Gol'tyapin Yu. V. Pavlovich V.K. Gal'chenko G.L. *Proc. Acad. Sci. U.S.S.R.* 1975 **224** 1122-1124
61. Subbotin O.A. Klimova T.V. Stanko V.I. Ustynyuk Yu.A. *J. Gen. Chem. U.S.S.R.* 1979 **49** 363-364
62. Johnson L.F. Jankowski W.C. "Carbon-13 NMR Spectra" Wiley-Interscience New York 1972
63. Breitmaier E. Haas G. Voelter W. "Atlas of Carbon-13 NMR Data" Vol. 1 and 2 Heyden and Son Ltd. London 1979

Solid State Nuclear Magnetic Resonance Spectroscopy

Solid state n.m.r. spectroscopy has been carried for information on their ^{11}B quadrupolar coupling constants[64], phase transitions[65,66,67] and molecular motions[68,69,70]. The use of solid state n.m.r. for carborane characterization has only recently been carried out with the help of magic angle spinning (MAS) techniques[71]. Solid state ^{11}B and ^{13}C n.m.r. spectra of parent carboranes proved to be of comparable quality to their solution state spectra. However a phenyl substituent is sufficiently bulky to interfere with the molecular reorientation resulting in extensively broadened signals.

^{13}C n.m.r. solid state spectroscopy has been carried out on carborane : proton sponge adducts using a Varian VXR-300 solid state nuclear magnetic resonance spectrometer. These adducts are either insoluble or sparingly soluble in deuterated solvents giving no or poor quality solution state ^{13}C n.m.r. spectra. Tetramethylsilane was referenced externally at 0.00 ppm in all solid state spectra produced in this study.

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65. Reyhardt E.C. Watton A. Petch H.E. *J. Magn. Reson.* 1982 **46** 453-468
66. Beckmann P. Wendel A. *J. Chem. Phys.* 1980 **73** 3514-3515
67. Beckmann P. Leffler A.J. *J. Chem. Phys.* 1980 **72** 4600-4607
68. Leffler A.J. Alexander M.N. Sagalyn P.L. Walker N. *J. Chem. Phys.* 1975 **63** 3971-3986
69. Reyhardt E.C. *J. Magn. Reson.* 1986 **69** 337-343
70. Leffler A.J. Alexander M.N. Sagalyn P.L. *J. Chem. Phys.* 1976 **65** 2650-2654
71. Harris R.K. Bowles J. Stephenson I.R. Wong E.H. *Spectrochim. Acta* 1988 **44A** 273-276

X-RAY CRYSTALLOGRAPHY

X-ray crystallography is an excellent tool for unambiguously determining the molecular structure of a compound in its solid state including its bond lengths and angles. However it requires adequate reflections produced from X-ray waves on the pure undistorted crystal of the compound of interest to determine its molecular structure. With carborane-containing compounds, X-ray studies cannot determine the positions of carbon atoms in a carborane cage as both carbon and boron atoms are similar in electron density so in this study aromatic rings bonded to carboranyl carbons were used to 'label' the cage carbon atoms.

The carborane crystals were mounted in Lindemann capillaries and X-ray irradiation on these crystals was carried out on a Stoe-Siemens diffractometer using CuK_{α} radiation (λ = 1.54184Å). ω/θ scan mode was used for data collecting with on-line profile fitting[72]. X-ray structures were determined using direct methods and difference syntheses with the help of computer programs[73] and international tables[74].

ULTRAVIOLET SPECTROSCOPY

Ultraviolet (uv) spectroscopy can be used to observe conjugation effects in certain carborane derivatives. A very weak cage absorption is seen between 240-270nm in parent carboranes but such absorptions are hidden in carborane derivatives containing aromatic rings as the benzene ring gives a strong band in the 220nm region and a weak band in the 240-280nm region[75,76]. Ultraviolet spectra of carborane derivatives were obtained on a Pye Unicam SP8-100 ultraviolet spectrophotometer with 899-221nm range and polarographic grade methanol was used as solvent.

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72. Clegg W. *Acta Cryst.* 1981 **A37** 22-28
73. Sheldrick G.M. SHELXTL. An integrated system for solving, refining and displaying crystal structures from diffraction data. Revision 5. University of Gottingen Germany 1985
74. "International Tables for X-ray Crystallography" Vol. IV Kynoch Press Birmingham p99-149
75. Leites L.A. Vinogradova L.E. Kalinin V.N. Zakharkin L.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1970 2437-2439
76. Wright J.R. Klingen T.J. *J. Inorg. Nucl. Chem.* 1970 **32** 2853-2861

ELEMENTAL ANALYSIS

All the carborane derivatives produced in this study were analysed for elemental carbon, hydrogen and nitrogen using a Carlo Erba Strumentazione Elemental Analyser Model 1106. Other elemental analyses were used for confirmation. Boron was determined by oxygen flask combustion followed by atomic absorption on a Perkin Elmer 5000 Atomic Absorption Spectrophotometer. Fluorine was analysed by bomb fusion with potassium of the sample followed by titration of the hydrogen fluoride after ion exchange. Iodine, bromine and chlorine were determined by oxygen flask combustion followed by potentiometric titration.

GAS CHROMATOGRAPHY

Gas chromatography is used to observe the number and ratio of compounds, including isomers, in solution or as pure liquid mixture[77]. In this study the number and ratio of isomers in a carborane isomer mixture in solution were determined on a Hewlett Packard 5890 Series II Gas Chromatograph, with crosslinked methyl silicone (SE30) column, flame ionization detector and nitrogen as carrier gas, if the isomers could not be separated by column or preparative thin layer chromatography. The percentage of peak area is assumed to be directly proportional to the percentage of isomer composition in this study. For each run carried out;

initial temperature = 40°C
rate = 10°C per min
final temperature = 270°C
final time = 20 min
temperature at injector = 200°C
temperature at detector = 275°C
sample size = 0.1μl
column size = 25m x 0.32mm x 0.25μm (length x outer diameter x inner diameter).

77. Loudon G.M. "Organic Chemistry" Addison-Wesley Reading (Massachusetts) 1984 p335-336

CHAPTER 4

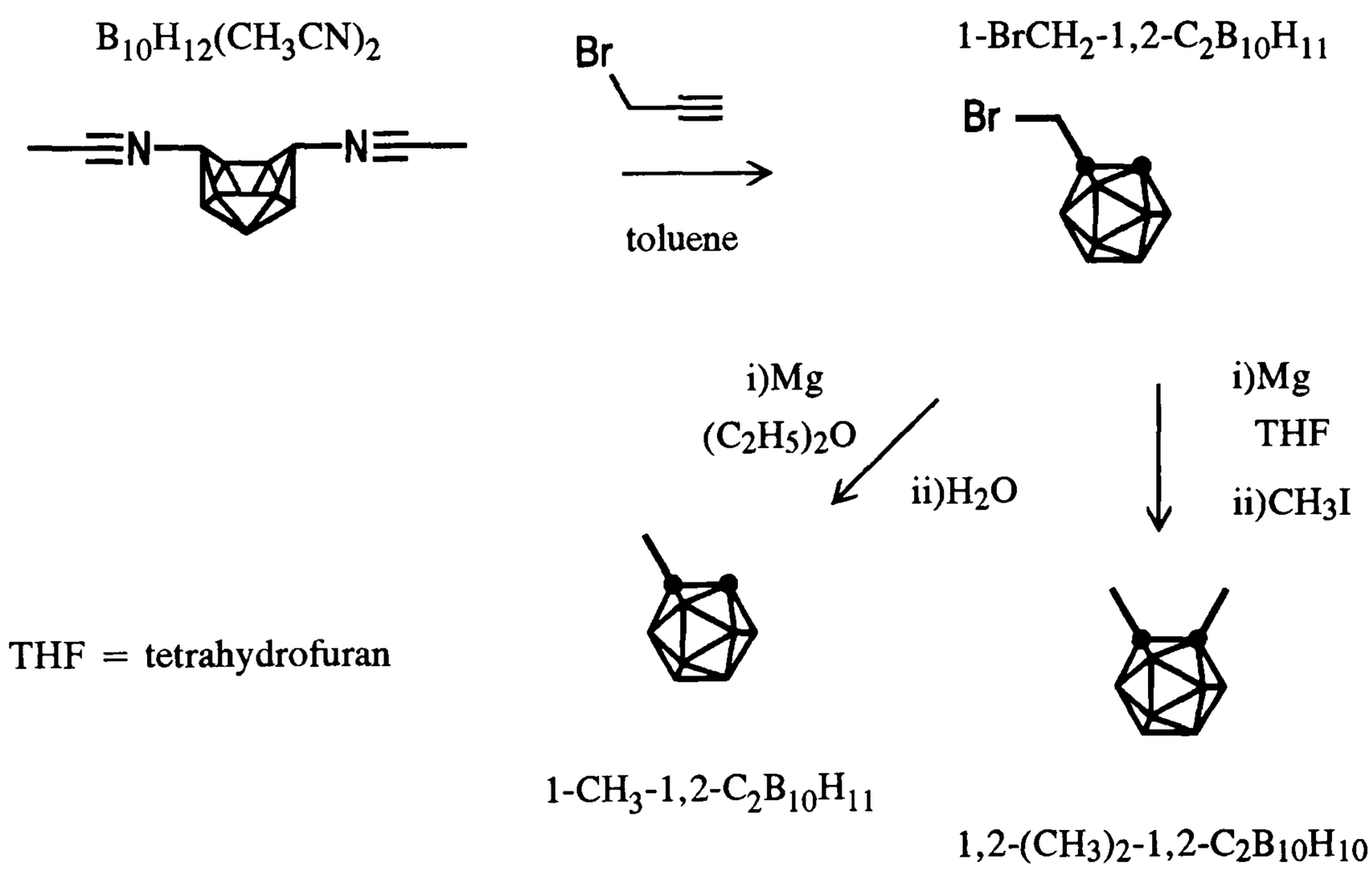
PREPARATION AND CHARACTERIZATION OF SOME C-SUBSTITUTED CARBORANES

PREPARATION AND CHARACTERIZATION OF SOME C-SUBSTITUTED CARBORANES

Crude *ortho*- and *meta*-carborane were obtained commercially for this study. Other starting carboranes used were prepared directly or indirectly from 6,9-bis(acetonitrile)-decaborane and substituted acetylenes.

1-methyl- and 1,2-dimethyl-*ortho*-carborane were made via 1-bromomethyl-*ortho*-carborane[1,2]. 1,2-diphenyl-, 1-phenyl- and 1-(4-methylphenyl)-*ortho*-carborane were produced directly from the appropriate substituted acetylene and 6,9-bis(acetonitrile)-decaborane. 1-phenyl-*meta*-carborane was obtained by thermal isomerization with amine degradation of the unchanged *ortho* isomer.

The experimental section in the next few pages shows the methods used and data obtained for the simple carborane intermediates produced. Experimental details of other carborane derivatives produced in this study are found at the end of chapters 5, 6, 7 and 8.



Preparations of 1-methyl- and 1,2-dimethyl-*ortho*-carborane.

1. Heying T.L. Ager J.W.Jr. Clark S.L. Mangold D.J. Goldstein H.L. Hillman M. Polak R.J. Szymanski J.W. *Inorg. Chem.* 1963 **2** 1089-1092

2. Fein M.M. Grafstein D. Paustian J.E. Bobinski J. Lichstein B.M. Mayes N. Schwartz N. Cohen M.S. *Inorg. Chem.* 1963 **2** 1115-1119

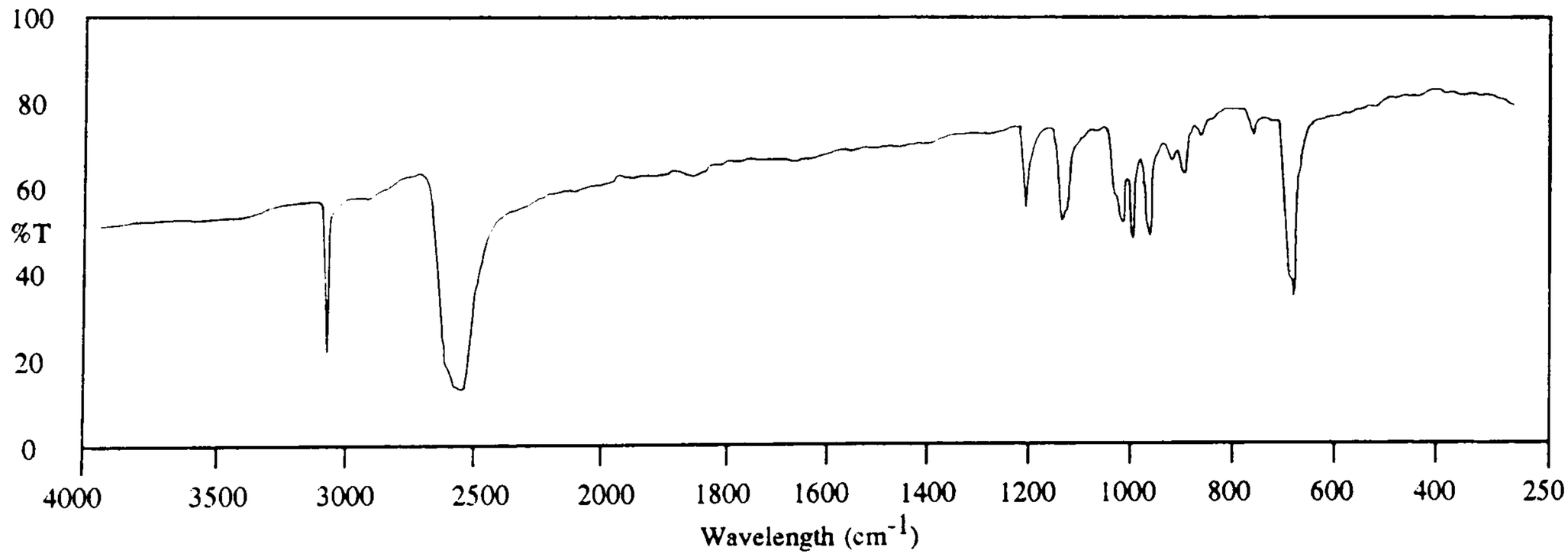
1,2-dicarba-*closo*-dodecaborane(12)

10g of crude *ortho*-carborane was vacuum sublimed at 100°C (0.001mmHg) using an oil bath to give 9.2g of pure *ortho*-carborane.

Melting point = 292-293°C (lit[1]. = 294.5-295.5°C)

Analysis Found: C,16.7; H,8.4. $C_2H_{12}B_{10}$ requires C,16.7; H,8.3.

Infrared (KBr disc; cm^{-1}) 3073(s), 2580(s), 1213(m), 1148(m), 1141(m), 1046(m), 1034(m), 1016(m), 984(m), 940(w), 917(w), 883(w), 782(w), 720(s), 717(s).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 146 corresponding to the species $^{12}C_2{}^{1}H_{12}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 140 and 146.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

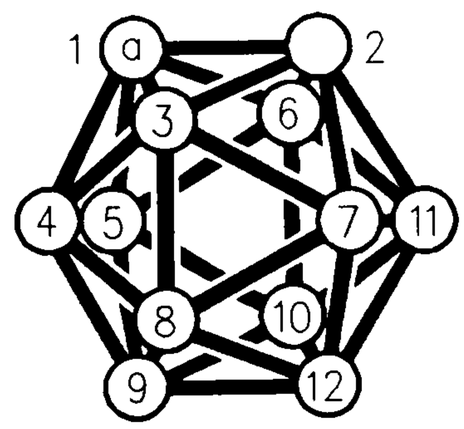
δ_{ppm}	intensity	type of peak	position of proton
3.70-1.00	10	broad multiplet	carboranyl B-H
3.56	2	broad singlet	carboranyl C-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron[3]
-3.80	2	9,12
-10.60	2	8,10
-15.00	4	4,5,7,11
-16.07	2	3,6

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
54.46	a



3. Venable T.L. Hutton W.C. Grimes R.N. *J. Am. Chem. Soc.* 1984 **106** 29-37

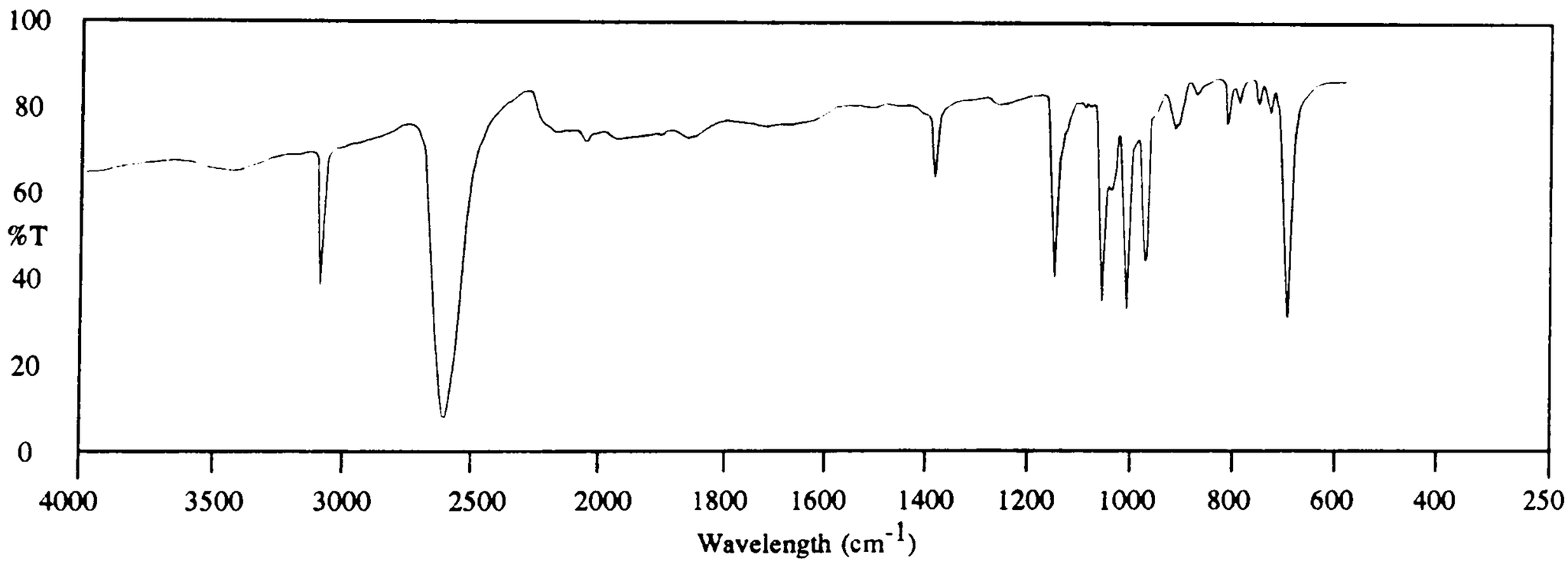
1,7-dicarba-*closo*-dodecaborane(12)

10g of crude *meta*-carborane was vacuum sublimed (0.001mmHg) using a boiling water bath to give 8.6g of pure *meta*-carborane.

Melting point = 262-263°C (lit.[4] = 265°C)

Analysis Found: C,16.6; H,8.2. $C_2H_{12}B_{10}$ requires C,16.7; H,8.3.

Infrared (KBr disc; cm^{-1}) 3062(m), 2605(s), 1387(w), 1162(m), 1072(m), 1056(w), 1027(m), 992(m), 940(w), 929(w), 897(w), 890(w), 834(w), 814(w), 777(w), 756(w), 722(m).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 146 corresponding to the species $^{12}C_2{}^{1}H_{12}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 140 and 146.

4. Grafstein D. Dvorak J. *Inorg. Chem.* 1963 **2** 1128-1133

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

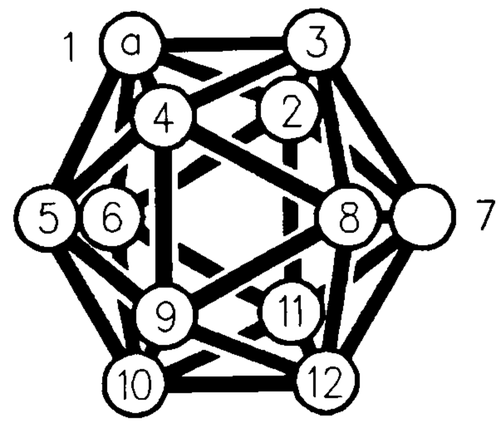
δ_{ppm}	intensity	type of peak	position of proton
2.63	2	broad singlet	carboranyl C-H
3.8-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron[3]
-6.43	2	5,12
-10.28	2	9,10
-13.06	4	4,6,8,11
-16.75	2	2,3

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
55.23	a



Decaborane(14)

Decaborane is a very hazardous material which can seriously affect the eyes, kidneys and central nervous system when its pungent odour is inhaled or by skin contact with its solid[5a]. If it is heated to 100°C, a violent explosion with evolution of large quantities of hydrogen usually occurs[6]. Decaborane slowly forms polymeric products if left to stand for weeks so purification is required before using the compound for reactions. It can be recrystallized from heptane but sublimation is prefered as exposure to personnel is greatly reduced. It can detonate by shock in halogenated solvents and some ethers like dioxane[1]. Decaborane(14) is best handled in a well-ventilated fume cupboard with disposable rubber gloves and a nickel spatula or in a glove box.

10g of crude decaborane(14) was vacuum sublimed under nitrogen at 70°C (0.001mmHg) with an oil bath and 8.3g of pure crystalline decaborane(14) was obtained. The sublimation apparatus was immersed in 1:1 methanol : water and left for 72 hours to destroy any residual decaborane.

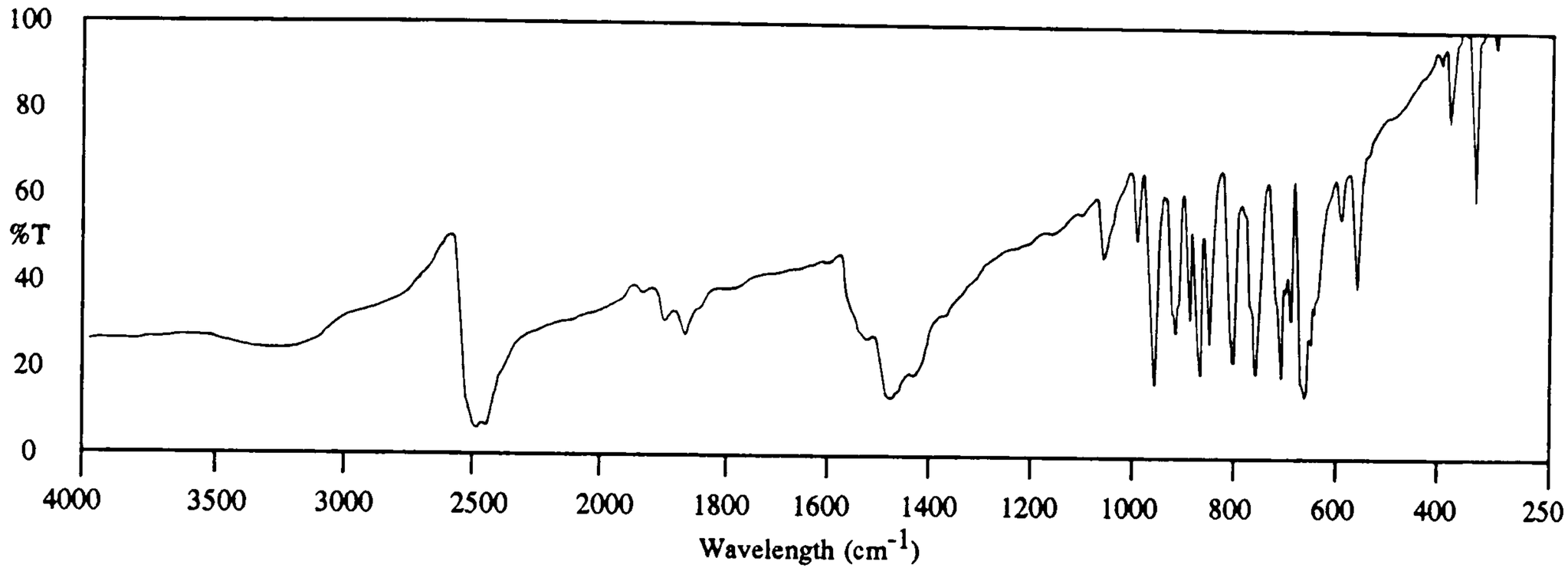
Melting point = 98.5-99°C (lit.[5b] = 99.7°C)

Analysis Found: H,11.4. $B_{10}H_{14}$ requires H,11.5.

5. Hughes R.L. Smith I.C. Lawless E.W. "Production of the Boranes and related research" (Ed. Holzmann R.T.) Academic Press New York 1967 a) p309 b) p190

6. Hawthorne M.F. Andrews T.D. Garrett P.M. Olsen F.P. Reintjes M. Tebbe F.N. Warren L.F. Wegner P.A. Young D.C. *Inorg. Syn.* 1967 10 91-118

Infrared (KBr disc; cm^{-1}) 2595(s), 2570(s), 2558(s), 2548(s), 2516(s), 2500(s), 1924(w), 1888(w), 1558(m), 1547(m), 1537(m), 1505(s), 1497(s), 1486(s), 1459(s), 1452(m), 1394(w), 1099(w), 1032(w), 1001(s), 967(m), 961(m), 958(m), 933(m), 914(s), 897(m), 858(m), 852(s), 828(w), 817(m), 808(s), 767(m), 760(s), 752(w), 741(m), 722(s), 715(s), 703(m), 695(m), 646(w), 613(m), 452(w), 438(w), 390(m), 349(w).



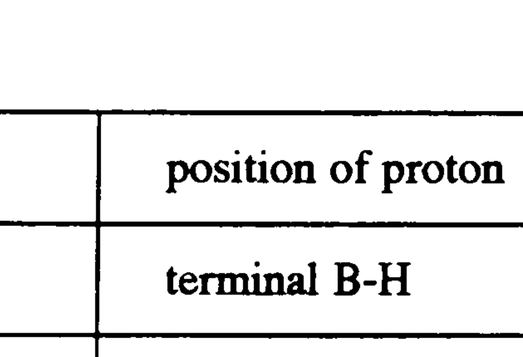
Mass spectrum (C.I.-) A highest mass peak was observed at m/e 124 corresponding to the species $^{11}B_{10}{}^{1}H_{14}$, accompanied with the usual boron isotope distribution between m/e 118 and 124.

^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

δ_{ppm}	intensity	type of peak	position of proton
4.92-0.08	10	broad multiplet	terminal B-H
-2.50	4	broad singlet	bridge B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent C_6D_6, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron[3]
12.02	2	1,3
10.49	2	6,9
0.00	4	5,7,8,10
-35.72	2	2,4



Each boron atom has a terminal hydrogen. Four bridge hydrogens are connected to (5 and 6), (6 and 7), (8 and 9) and (9 and 10) boron atoms.

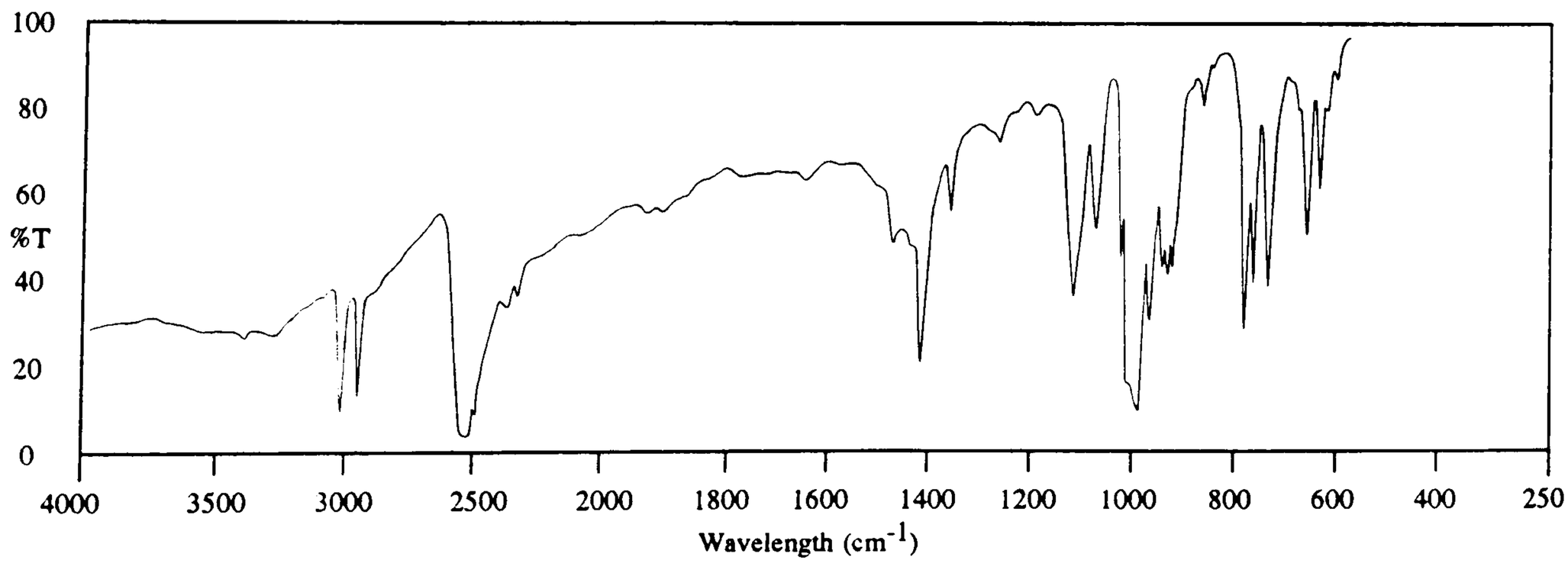
6,9-bis(acetonitrile)-decaborane

In this study decaborane is stored as its bis(ligand) complex to eliminate the need for its constant resublimation.

In the fume cupboard, 18.3g (0.15 moles) sublimed decaborane was dissolved in 100ml dry acetonitrile and heated slowly with stirring to 80°C under a nitrogen atmosphere with hydrogen gas evolution. After three hours, the white precipitate formed was filtered off and washed with fresh dry acetonitrile. The solid was vacuum dried and identified as 28.3g (93.4%) 6,9-bis(acetonitrile)-decaborane. All apparatus used in this method were left in 1 : 1 methanol : water for 48 hours to degrade any toxic decaborane present.

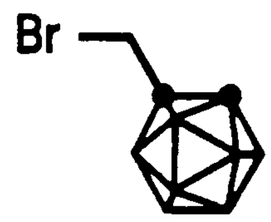
Analysis Found: C,23.6; H,8.7; N,13.8. $C_4H_{18}B_{10}N_2$ requires C,23.8; H,8.9; N,13.9.

Infrared (KBr disc; cm^{-1}) 2980(s), 2977(s), 2915(s), 2510(s), 2502(s), 2478(s), 2379(w), 2366(w), 2324(w), 1459(w), 1451(w), 1437(w), 1426(w), 1403(m), 1356(w), 1351(w), 1261(w), 1192(w), 1119(m), 1111(m), 1078(m), 1030(m), 1014(s), 1002(s), 995(s), 974(m), 951(m), 940(m),875(w), 858(w), 793(m), 778(m), 749(m), 692(w), 676(m), 652(m), 639(w), 620(w).



Mass spectrum (C.I.-) A highest mass peak was observed at m/e 123 corresponding to the fragment $^{1}H_{11}{}^{11}B_{10}$, accompanied by the boron isotope distribution between m/e 118 and 123. A peak of m/e 40 was also present corresponding to $^{12}C_2{}^{1}H_2{}^{14}N$ fragment from acetonitrile ligands.

1-bromomethyl-1,2-dicarba-*closo*-dodecaborane(12)

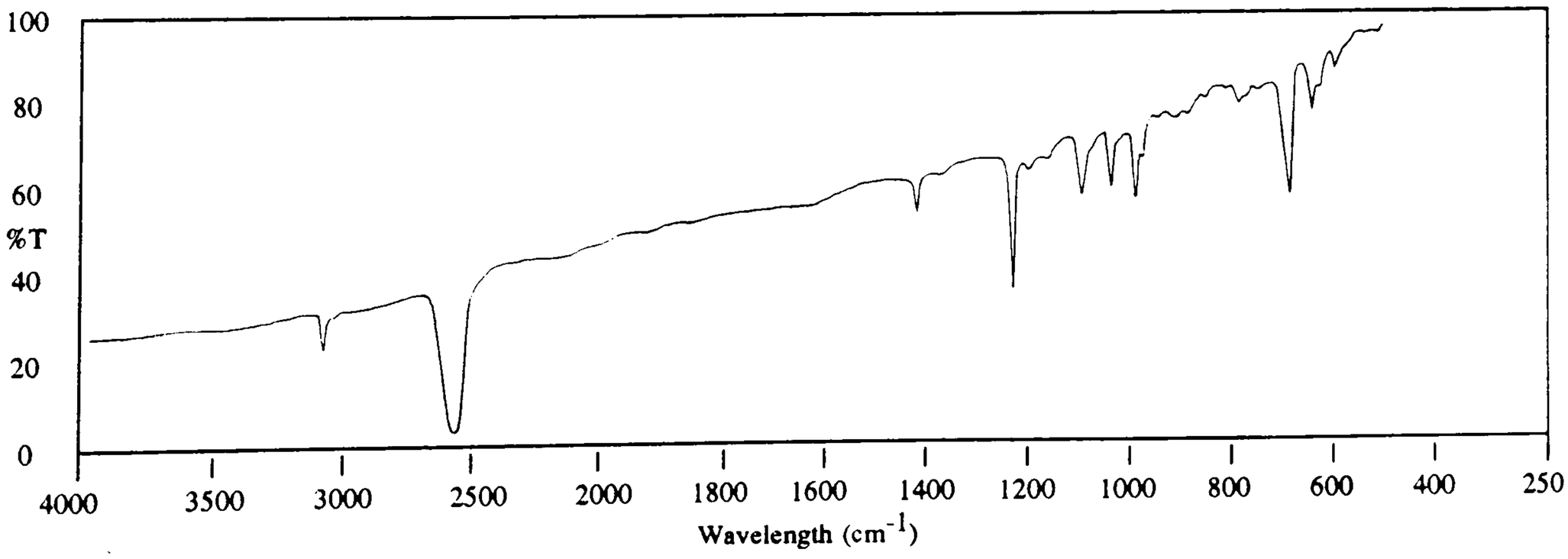


A solution of 5.95g (0.05 moles) 3-bromopropyne in 11.9ml of dry toluene was added slowly to a vigorously stirred slurry of 10.1g (0.05 moles) of 6,9-bis(acetonitrile)-decaborane in 60ml dry toluene under nitrogen. The mixture was slowly heated to refluxing producing gas bubbles and left to reflux for 24 hours. After cooling the solvents were removed by rotary evaporator and *in vacuo*. The residue was extracted five times with hexane. The combined extracts were washed with 10% aqueous sodium hydroxide then distilled water and dried over anhydrous magnesium sulphate. The organic layer was filtered and after removing hexane by rotary evaporator the oil was vacuum distilled to give 8.7g (73.4%) of 1-bromomethyl-*ortho*-carborane.

Melting point = 31-32°C (lit[6]. = 33°C)

Analysis Found: C,14.9; H,5.6. $C_3H_{13}B_{10}Br$ requires C,15.2; H,5.5.

Infrared (KBr disc; cm^{-1}) 3072(m), 3034(w), 2597(s), 2585(s), 1430(w), 1250(m), 1222(w), 1191(w), 1121(w), 1104(w), 1062(w), 1017(w), 1006(w), 972(w), 946(w), 937(w), 917(w), 882(w), 843(w), 820(w), 782(w), 722(m), 680(w), 666(w), 636(w).



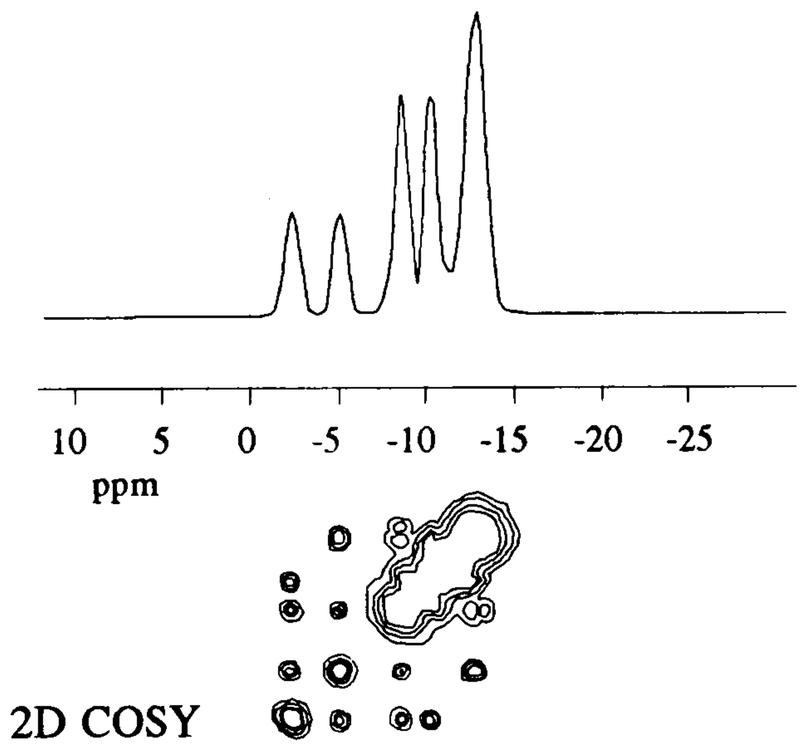
Mass spectrum (E.I.) A highest mass peak was observed at m/e 239 corresponding to the species $^{12}C_3{}^{1}H_{13}{}^{11}B_{10}{}^{80}Br$, accompanied by the usual carborane isotope distribution pattern between m/e 233 and 239.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
3.99	1	broad singlet	carboranyl C(c)-H
3.96	2	singlet	methyl C(a)-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

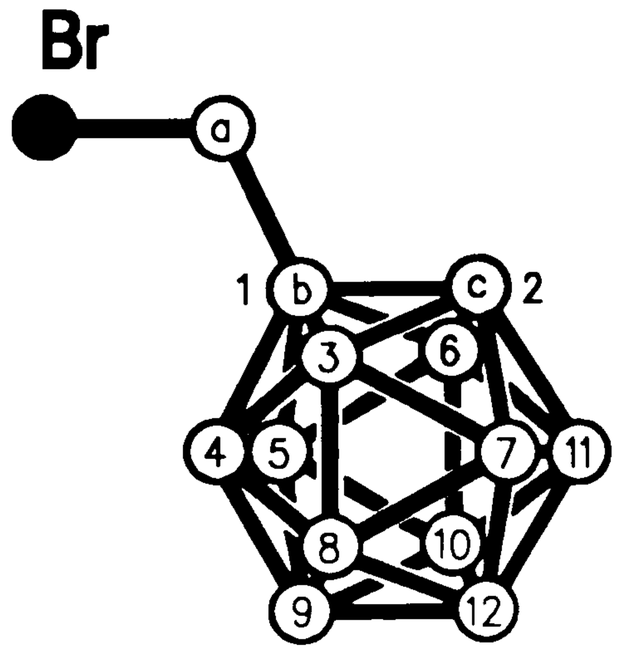
δ_{ppm}	intensity	position of boron
-2.54	1	9
-5.32	1	12
-8.82	2	8,10
-10.67	2	4,5
-12.86	4	3,6,7,11



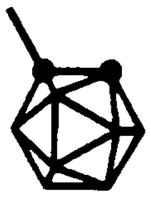
2D COSY

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
71.18	b
60.94	c
32.16	a



1-methyl-1,2-dicarba-*closo*-dodecaborane(12)

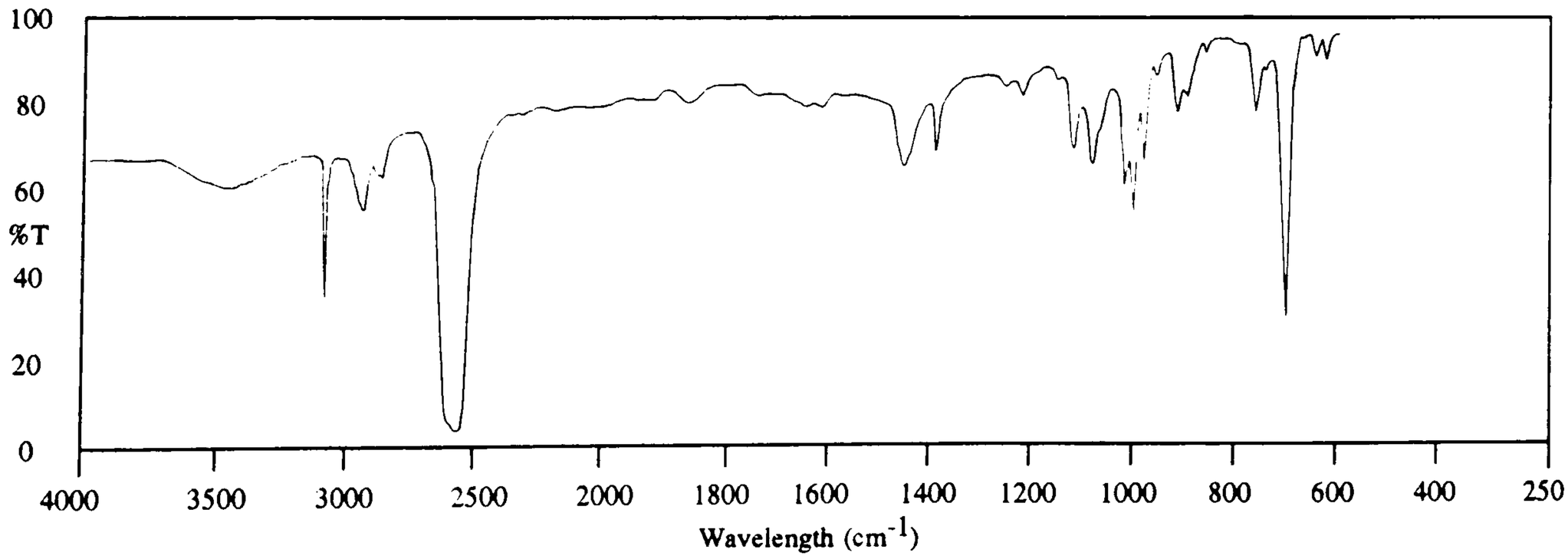


0.73g (0.03 moles) of dry magnesium turnings and 20ml diethyl ether were heated to 30°C under dry nitrogen atmosphere and 5.93g (0.025 moles) 1-bromomethyl-*ortho*-carborane in 30ml anhydrous diethyl ether was added dropwise. After three hours refluxing the solution was cooled and poured into 100ml ice-cold water. The mixture was acidified with 1:1 hydrochloric acid : water and the aqueous layer was extracted with diethyl ether in three 20ml portions. The combined ether extracts were dried with anhydrous magnesium sulphate, filtered and the ether was removed using a rotary evaporator leaving a residue which was vacuum sublimed giving 3.35g (84.8%) white solid identified as 1-methyl-*ortho*-carborane.

Melting point = 214-215°C (lit[7]. = 218-219°C)

Analysis Found: C,22.6; H,8.8. $C_3H_{14}B_{10}$ requires C,22.8; H,8.9.

Infrared (KBr disc; cm^{-1}) 3067(m), 2962(w), 2947(w), 2936(w), 2874(w), 2858(w), 2608(s), 2589(s), 2581(s), 2576(s), 1459(m), 1452(m), 1440(m), 1391(m), 1259(w), 1228(w), 1175(w), 1130(m), 1094(m), 1083(m), 1032(m), 1016(m), 997(m), 987(w), 983(w), 933(w), 914(w), 901(w), 880(w), 8244(w), 813(w), 785(w), 767(w), 760(w), 720(s), 672(w), 669(w), 652(w), 488(w).



7. Grafstein D. Bobinski J. Dvorak J. Smith H. Schwartz N. Cohen M.S. Fein M.M. *Inorg. Chem.* 1963 **2** 1120-1125

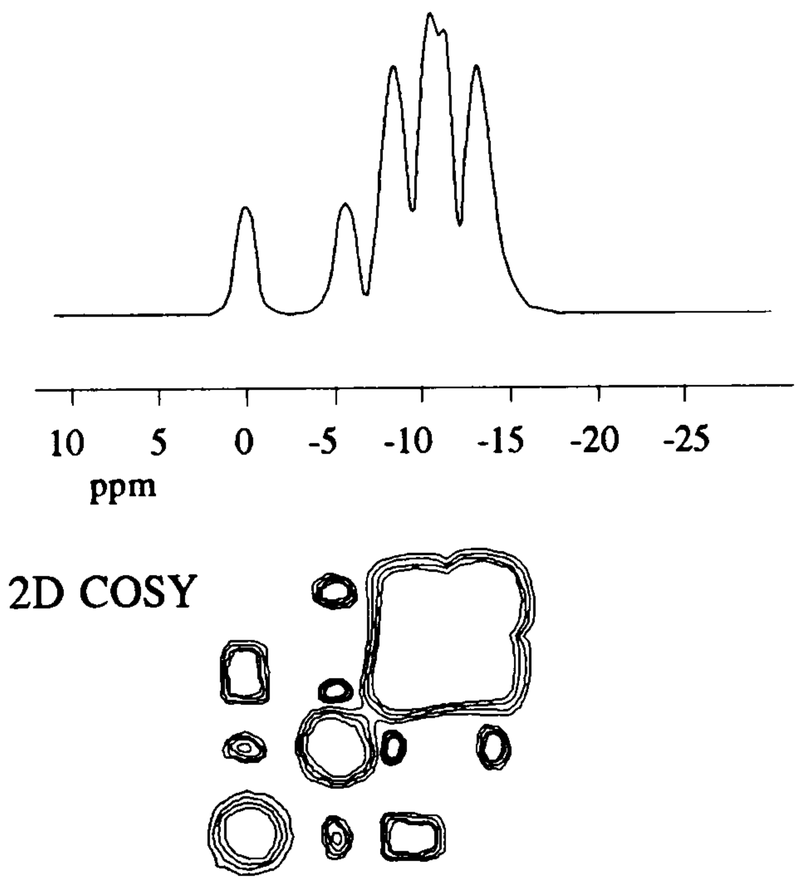
Mass spectrum (E.I.) A highest mass peak was observed at m/e 160 corresponding to the species $^{12}C_3{}^{1}H_{14}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 154 and 160.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
3.59	1	broad singlet	carboranyl C(c)-H
2.02	3	singlet	methyl C(a)-H
3.8-1.0	10	broad multiplet	carboranyl B-H

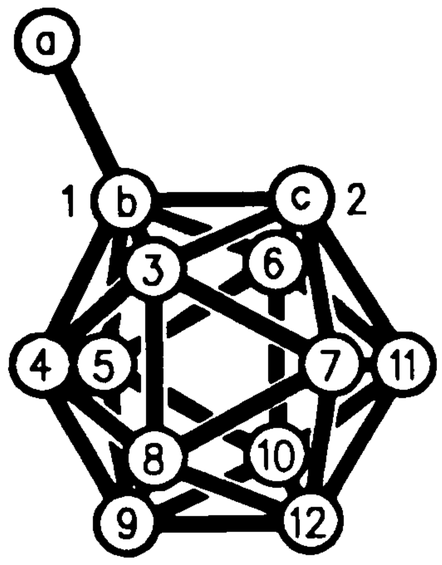
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-1.80	1	9
-6.75	1	12
-9.17	2	8,10
-10.64	2	4,5
-11.17	2	3,6
-12.68	2	7,11



^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
71.50	b
62.16	c
26.47	a



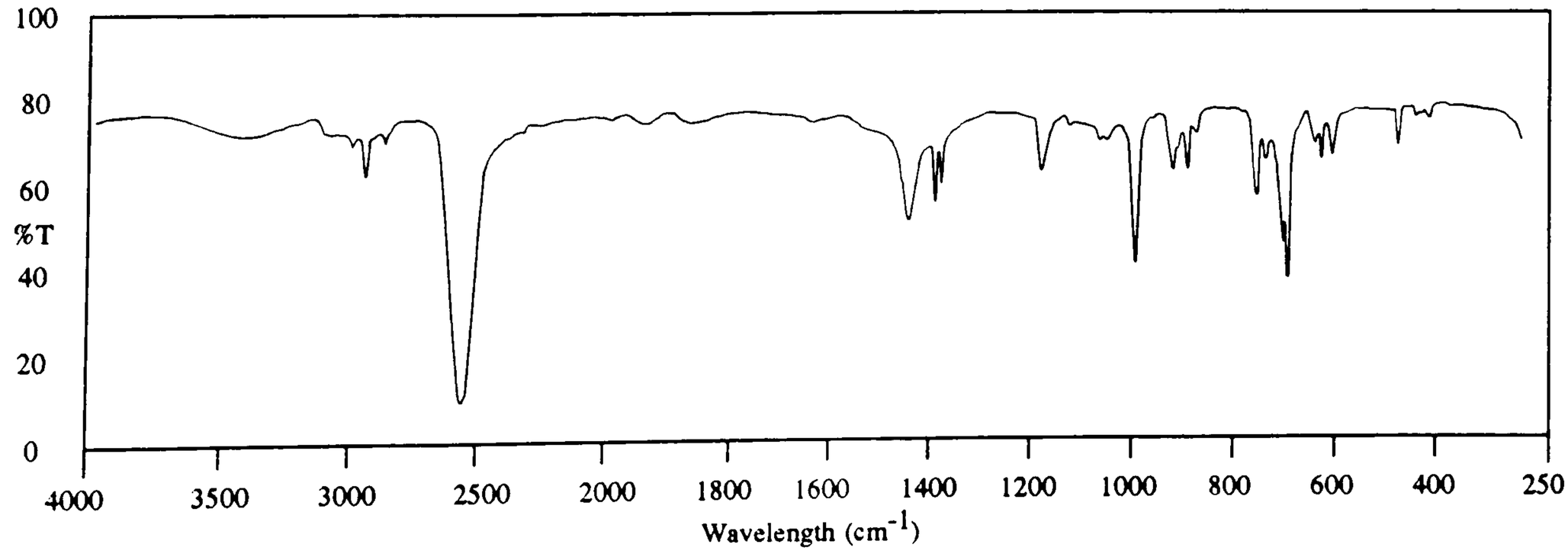
1,2-dimethyl-1,2-dicarba-*closo*-dodecaborane(12)

6.08g (0.25 moles) dry magnesium turnings in 20ml dry tetrahydrofuran was treated dropwise with 4.74g (0.2 moles) 1-bromomethyl-*ortho*-carborane in 50ml dry tetrahydrofuran under a nitrogen atmosphere. The solution was refluxed for three hours and then cooled. After filtering off the excess magnesium metal, the solution was treated dropwise with 4.97g (0.35 moles) of methyl iodide and then refluxed for two hours. At ambient temperature the solution was slowly added with stirring to 100ml of dilute 2M hydrochloric acid and the aqueous layer was washed with three 20ml portions of diethyl ether. The combined extracts were washed with distilled water and dried over anhydrous magnesium sulphate. After removing the ether by rotary evaporator the residue was recrystallized from absolute ethanol to give 2.8g (81.4%) of 1,2-dimethyl-*ortho*-carborane.

Melting point = 261-262°C (lit[8]. = 265°C)

Analysis Found: C,27.1; H,9.4. $C_4H_{16}B_{10}$ requires C,27.9; H,9.3.

Infrared (KBr disc; cm^{-1}) 2995(w), 2941(m), 2863(w), 2575(s), 1440(m), 1395(w), 1382(m), 1192(m), 1139(w), 1082(w), 1069(w), 1019(s), 946(m), 935(w), 918(m), 900(w), 782(m), 769(w), 740(m), 735(m), 727(s), 671(w), 660(w), 639(w), 511(w), 478(w), 469(w), 451(w).



8. Zakharkin L.I. Brattsev V.A. Chapovskii Yu. A. *J. Gen. Chem. U.S.S.R.* 1965 **35** 2149-2155

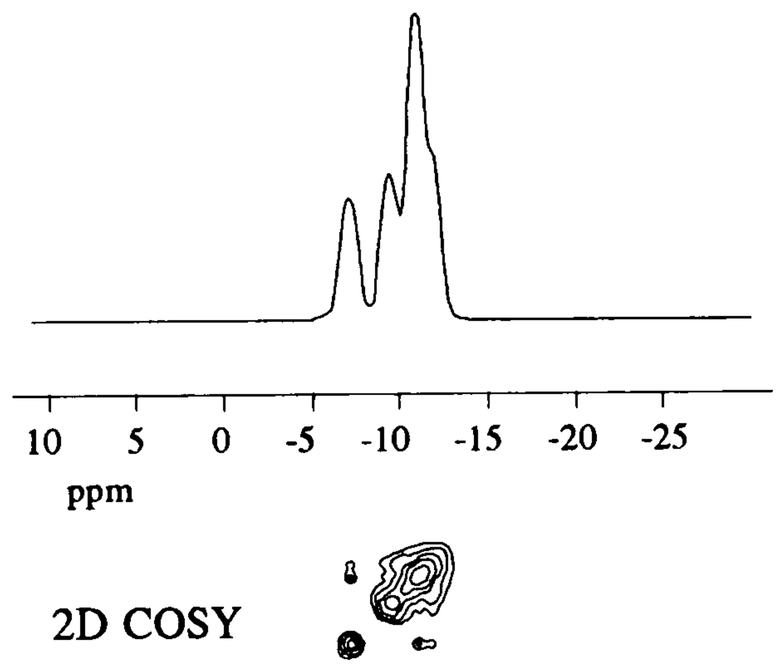
Mass spectrum (E.I.) A highest mass peak was observed at m/e 174 corresponding to the species $^{12}C_4{}^{1}H_{16}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 168 and 174.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
2.02	6	singlet	methyl C(a)-H
4.0-0.9	10	broad multiplet	carboranyl B-H

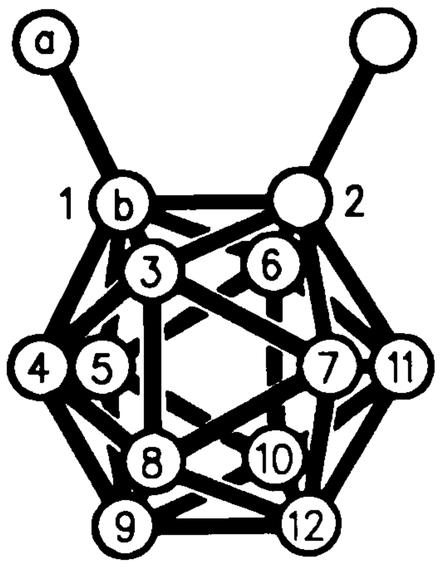
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-6.61	2	9,12
-9.61	2	3,6
-10.92	4	4,5,7,11
-11.66	2	8,10

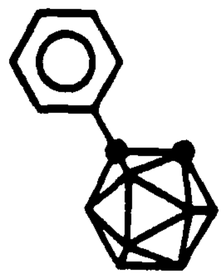


^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
73.37	b
23.16	a



1-phenyl-1,2-dicarba-*closo*-dodecaborane(12)

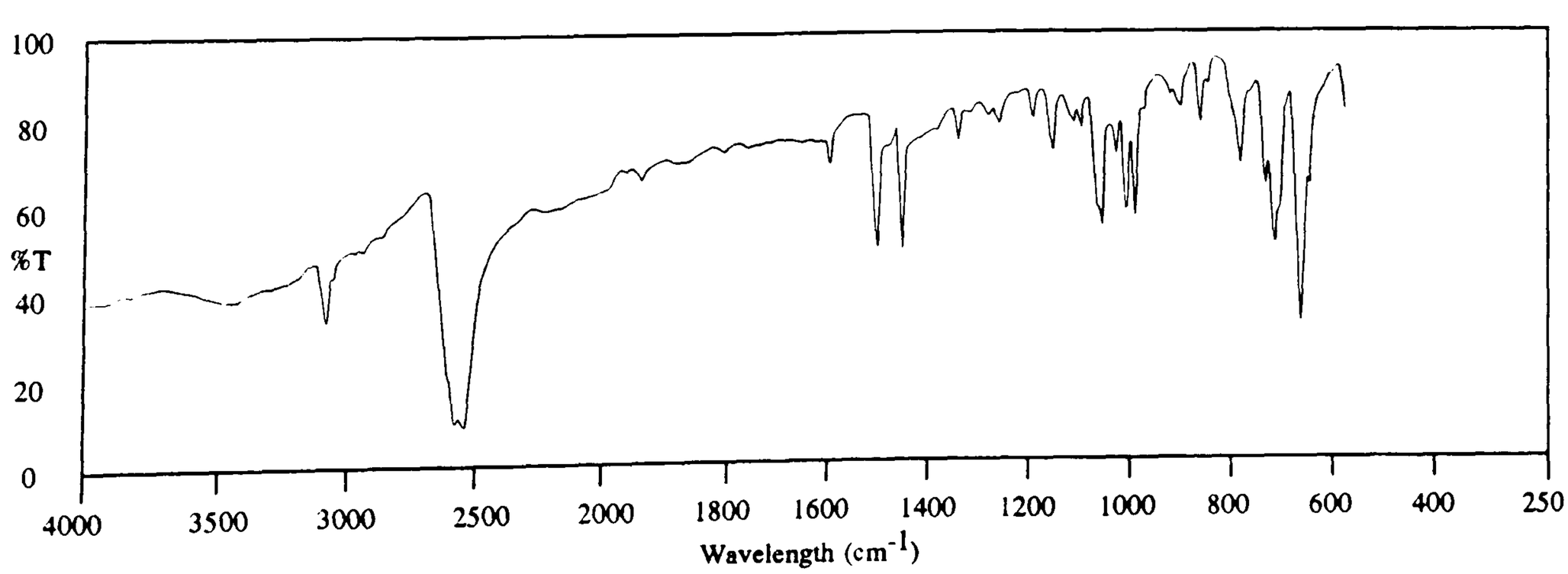


10.2g (0.1 moles) of freshly distilled phenylacetylene in 60ml anhydrous toluene was added to a stirred slurry of 20.2g (0.1 moles) 6,9-bis(acetonitrile)-decaborane and 60ml toluene under nitrogen. The mixture was heated gradually to refluxing temperature when gas evolution was observed. The orange solution was refluxed for 24 hours, cooled and 30ml of methanol added giving hydrogen gas from unreacted decaborane. After 12 hours stirring, the solvents were removed by rotary evaporator and *in vacuo* leaving a viscous oil. The residue was vacuum distilled to give a low melting solid which was dissolved in methanol to ensure complete degradation of any decaborane residues. The methanol was removed under vacuum and the residue recrystallized from hexane to give 11.1g (50.5%) crystals of 1-phenyl-*ortho*-carborane.

Melting point = 67-68°C (lit[2]. = 69.5-70°C)

Analysis Found: C,43.8; H,7.3. $C_8H_{16}B_{10}$ requires C,43.6; H,7.3.

Infrared (KBr disc; cm^{-1}) 3110(w), 3066(s), 3052(w), 2938(w), 2910(m), 2855(w), 2611(s), 2600(s), 2586(s), 2574(s), 2554(s), 1947(w), 1862(w), 1791(w), 1711(w), 1648(w), 1600(w), 1583(w), 1498(m), 1462(w), 1451(m), 1378(w), 1341(w), 1317(w), 1281(w), 1260(w), 1222(w), 1198(w), 1161(m), 1120(w), 1107(w), 1071(m), 1039(w), 1021(m), 1004(m), 983(w), 935(w), 920(w), 913(w), 876(w), 861(w), 832(w), 812(w), 800(m), 778(w), 750(m), 733(s), 710(w), 696(m), 687(m), 681(m), 668(m), 601(w), 592(w), 584(w), 563(m), 528(w), 488(m), 459(w), 452(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 222 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 216 and 222.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

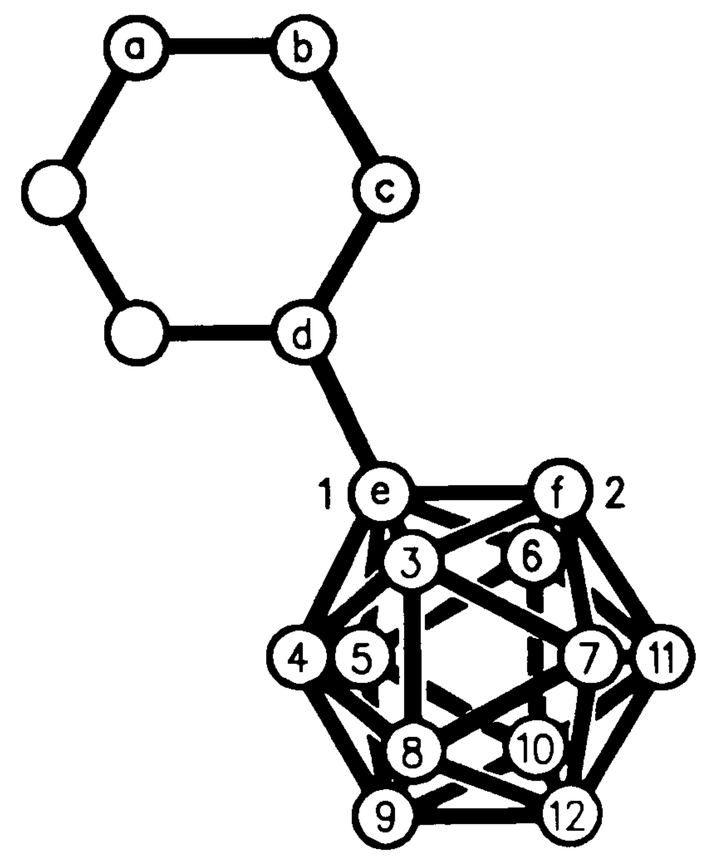
δ_{ppm}	intensity	type of peak	position of proton
7.50-7.47 7.43-7.30	5	multiplet	aromatic C(a,b,c)-H
3.97	1	broad singlet	carboranyl C(f)-H
4.0-1.1	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

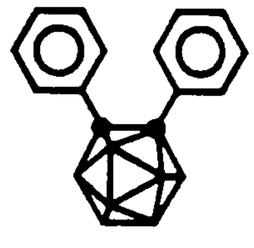
δ_{ppm}	intensity	position of boron
-2.05	1	9
-4.36	1	12
-9.05	2	8,10
-11.01	4	4,5,3,6
-12.84	2	7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
133.39	d
129.85	b
128.79	a
127.45	c
76.50	e
60.13	f



1,2-diphenyl-1,2-dicarba-*closo*-dodecaborane(12)

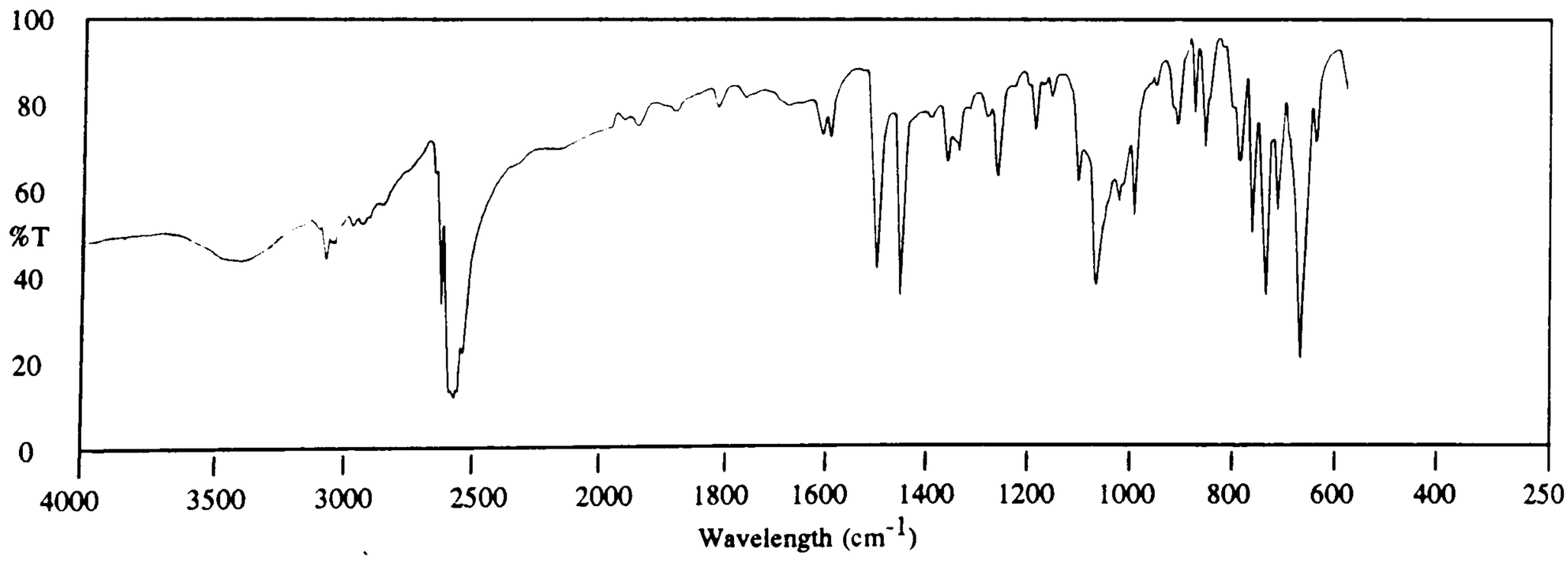


8.9g (0.05 moles) of diphenylacetylene in 40ml dry toluene was added to a slurry of 10.1g (0.05 moles) 6,9-bis(acetonitrile)-decaborane in 30ml anhydrous toluene with stirring under a nitrogen atmosphere. The mixture was heated cautiously to refluxing with hydrogen evolving. After 24 hours refluxing, the dark red solution was cooled to room temperature, 40ml methanol added and left to stir for 12 hours. The solvents were removed by rotary evaporator then *in vacuo* leaving a dark brown solid which was ground to a powder. The powder was extracted in a soxhlet apparatus with hexane for 24 hours. Hexane was driven off by rotary evaporator leaving a yellow solid which was recrystallized from hexane producing 10.7g (72.3%) of 1,2-diphenyl-*ortho*-carborane.

Melting point = 146-147°C (lit[10]. = 148-149°C)

Analysis Found: C,56.9; H,6.8. $C_{14}H_{20}B_{10}$ requires C,56.7; H,6.8.

Infrared (KBr disc; cm^{-1}) 3108(w), 3091(w), 3060(w), 3041(w), 3026(w), 2962(w), 2924(w), 2900(w), 2853(w), 2662(w), 2638(m), 2598(s), 2584(s), 2571(s), 2551(s), 1958(w), 1885(w), 1802(w), 1750(w), 1592(w), 1578(w), 1490(m), 1447(m), 1385(w), 1355(w), 1341(w), 1333(w), 1314(w), 1279(w), 1260(m), 1229(w), 1199(w), 1189(w), 1173(w), 1158(w), 1108(m), 1075(m), 1062(m), 1053(m), 1031(m), 1023(m), 1002(m), 960(w), 927(w), 920(w), 889(w), 870(w), 836(w), 815(w), 802(w), 780(m), 756(s), 730(m), 690(s), 658(w), 599(w), 580(m), 512(w).



9. Stanko V.I Babuskina T.A. Khrapov V.V. Koreshkov Yu.D. Klimova A.I. Alymov A.M. Vasil'ev A.M. *J. Gen. Chem. U.S.S.R.* 1977 **47** 360-368

10. Stanko V.I. Kopylov V.V. Klimova A.I. *J. Gen. Chem. U.S.S.R.* 1965 **35** 1437-1439

Mass spectrum (E.I.) A highest mass peak was observed at m/e 298 corresponding to the species $^{12}C_{14}{}^{1}H_{20}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 292 and 298.

^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

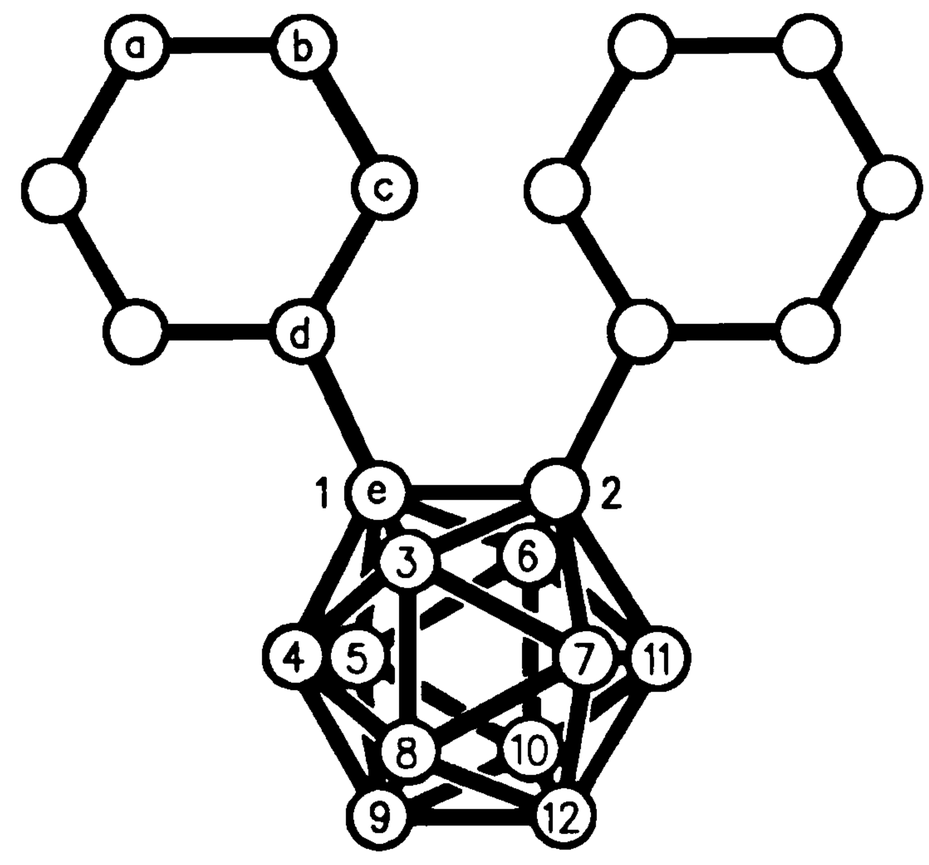
δ_{ppm}	intensity	type of peak	position of proton
7.19-7.12 6.70-6.56	10	multiplet	aromatic C(a,b,c)-H
4.0-0.9	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm. Peak assignments were based on peak shapes.

δ_{ppm}	intensity	position of boron
-3.88	2	9,12
-10.65	4	4,5,7,11
-11.81	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
130.56	c
130.12	a
128.22	b
85.21	e



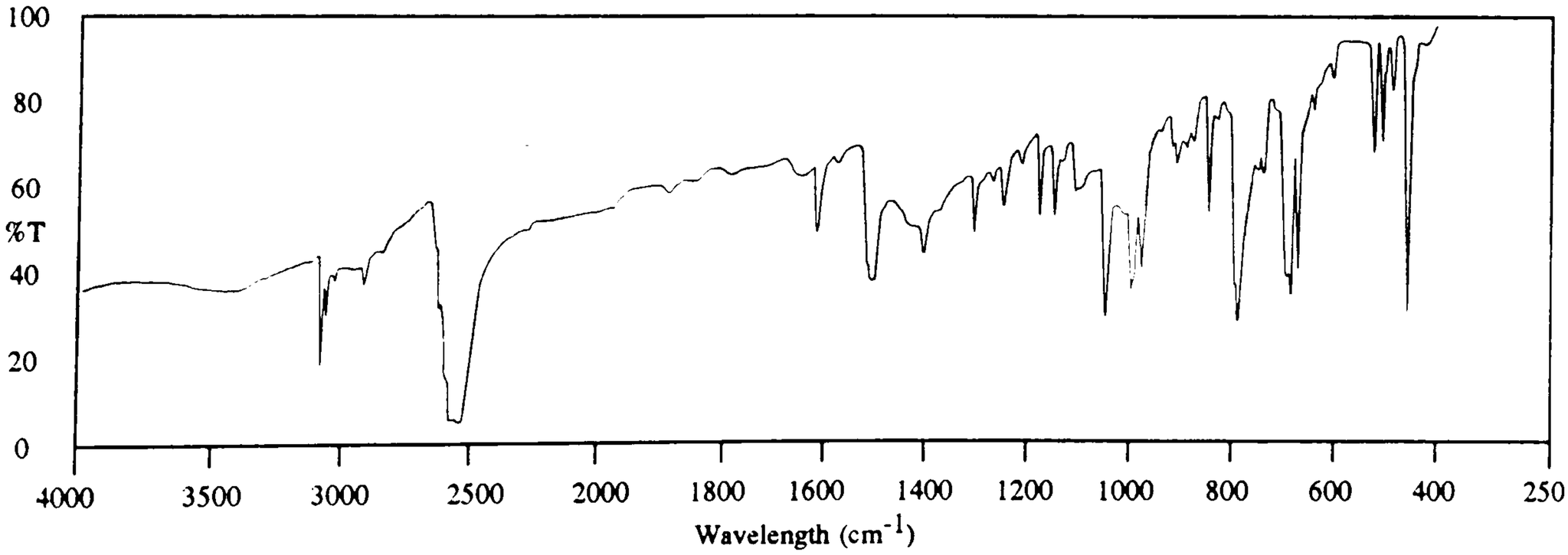
1-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane(12)

5.7g (0.05 moles) of freshly distilled 4-methylphenylacetylene in 60ml dry toluene was added to a stirred slurry of 10.1g (0.05 moles) 6,9-bis(acetonitrile)-decaborane and 60ml anhydrous toluene under nitrogen. The mixture was heated gradually to refluxing temperature where gas evolution was observed. The red solution was refluxed for 24 hours, cooled and 30ml of methanol added giving hydrogen gas from unreacted decaborane. After 12 hours stirring, the solvents were removed by rotary evaporator and *in vacuo* leaving a solid which was ground to a powder and extracted with boiling hexane in a soxhlet apparatus. The hexane was removed from the extract by rotary evaporator and the yellow residue was recrystallized from methanol to give 6.8g (58.1%) white crystals of 1-(4-methylphenyl)-*ortho*-carborane.

Melting point = 152-153°C (lit[11]. = 155°C)

Analysis Found: C,47.0; H,8.1. $C_9H_{18}B_{10}$ requires C,46.2; H,7.7.

Infrared (KBr disc; cm^{-1}) 3069(m), 3055(m), 3037(w), 2982(w), 2916(w), 2545(s), 1611(w), 1508(m), 1503(m), 1437(w), 1410(m), 1318(w), 1282(w), 1259(w), 1229(w), 1194(w), 1167(w), 1153(w), 1129(w), 1121(w), 1069(m), 1034(w), 1021(m), 1002(m), 942(w), 935(w), 918(w), 904(w), 876(m), 864(w), 819(s), 781(w), 770(w), 727(m), 719(s), 706(m), 674(w), 561(w), 547(w), 524(w), 498(m), 463(w).



11. Zakharkin L.I. Kalinin V.N. Shepilov I.P. *Dokl. Akad. Nauk. S.S.S.R.* 1967 **174** 606-9 (Russ) [CA68:39684e]

Mass spectrum (E.I.) A highest mass peak was observed at m/e 236 corresponding to the species $^{12}C_9{}^{1}H_{18}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 230 and 236.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

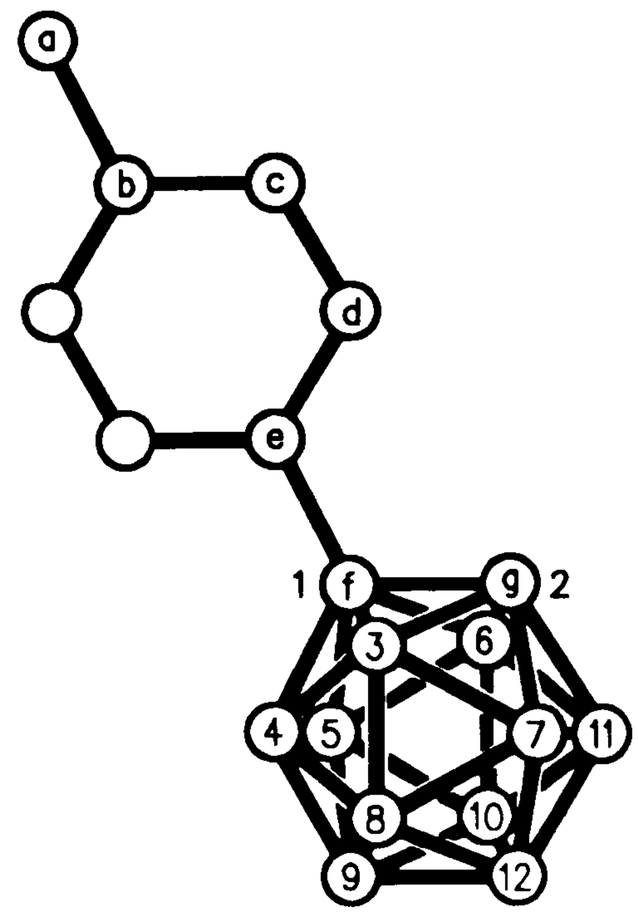
δ_{ppm}	intensity	type of peak	position of proton
7.41 7.38 7.17 7.14	4	doublet of doublets	aromatic C(c,d)-H
3.95	1	broad singlet	carboranyl C(g)-H
2.37	3	singlet	methyl C(a)-H
4.1-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

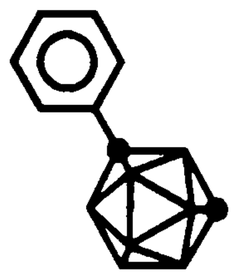
δ_{ppm}	intensity	position of boron
-1.98	1	9
-4.28	1	12
-8.89	2	8,10
-10.88	4	4,5,3,6
-12.75	2	7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
140.17	b
129.44	d,e
127.47	c
76.70	f
60.36	g
20.94	a



1-phenyl-1,7-dicarba-*closo*-dodecaborane(12)



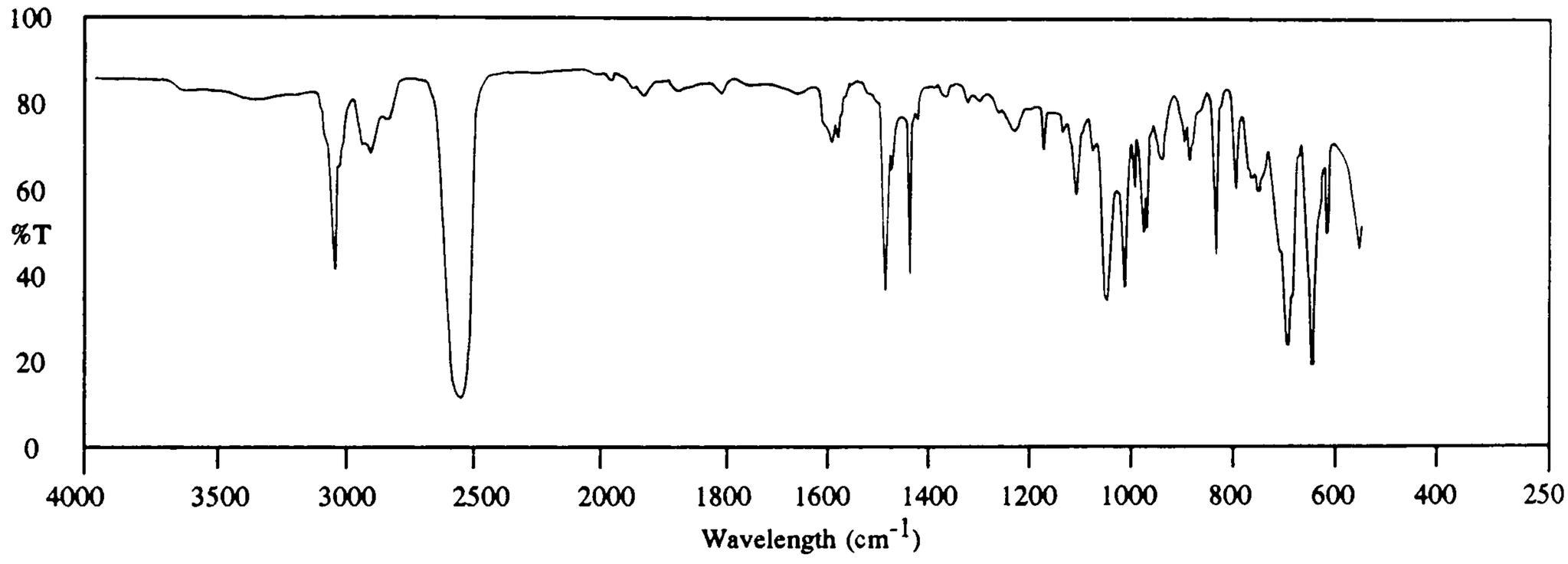
A 16mm bore Carius tube (200mm length) was charged with 2.2g (0.01 moles) of 1-phenyl-*ortho*-carborane and sealed with a blow torch under vacuum. The tube was placed inside a steel jacket and heated in a furnace to 420°C for 24 hours. The tube was cooled to ambient temperature and then carefully opened in the fume hood by glass scratching. The contents were removed from the tube with the help of boiling hexane into a beaker. The cloudy solution was filtered and the hexane was removed from the filtrate by rotary evaporator leaving an oil. Thin layer chromatography showed the oil to contain two compounds, one found to be the starting material. The oil was dissolved in 30ml dry hexane and mixed with 3ml piperidine. The mixture was refluxed for three hours, cooled and extracted with two molar hydrochloric acid. The colourless hexane solution was separated, washed with distilled water, dried over anhydrous magnesium sulphate and filtered. Hexane was pumped off by rotary evaporator leaving a residue which was vacuum distilled to give 1.6g (72.7% conversion) of 1-phenyl-*meta*-carborane.

Melting point = 53-54°C (lit[12]. = 55-55.5°C)

Analysis Found: C,43.8; H,7.5. $C_8H_{16}B_{10}$ requires C,43.6; H,7.3.

12. Hawthorne M.F. Young D.C. Garrett P.M. Owen D.A. Schwerin S.G. Tebbe F.N. Wegner P.A. *J. Am. Chem. Soc.* 1968 **90** 862-868

Infrared (KBr disc; cm^{-1}) 3110(w), 3091(w), 3063(m), 3042(w), 3038(w), 2958(w), 2924(w), 2869(w), 2857(w), 2615(s), 2605(s), 2598(s), 2590(s), 1953(w), 1803(w), 1611(w), 1608(w), 1600(w), 1597(w), 1585(w), 1498(m), 1486(w), 1451(m), 1445(w), 1436(w), 1385(w), 1342(w), 1324(w), 1320(w), 1283(w), 1255(w), 1248(w), 1198(w), 1163(w), 1139(w), 1109(w), 1084(m), 1081(m), 1050(m), 1031(w), 1012(m), 1006(m), 1000(w), 991(w), 983(w), 978(w), 942(w), 938(w), 927(w), 924(w), 912(w), 907(w), 878(m), 870(w), 839(w), 816(w), 810(w), 797(w), 790(w), 787(w), 756(m), 742(s), 733(m), 721(w), 702(m), 697(s), 692(s), 668(m), 607(m), 580(m).



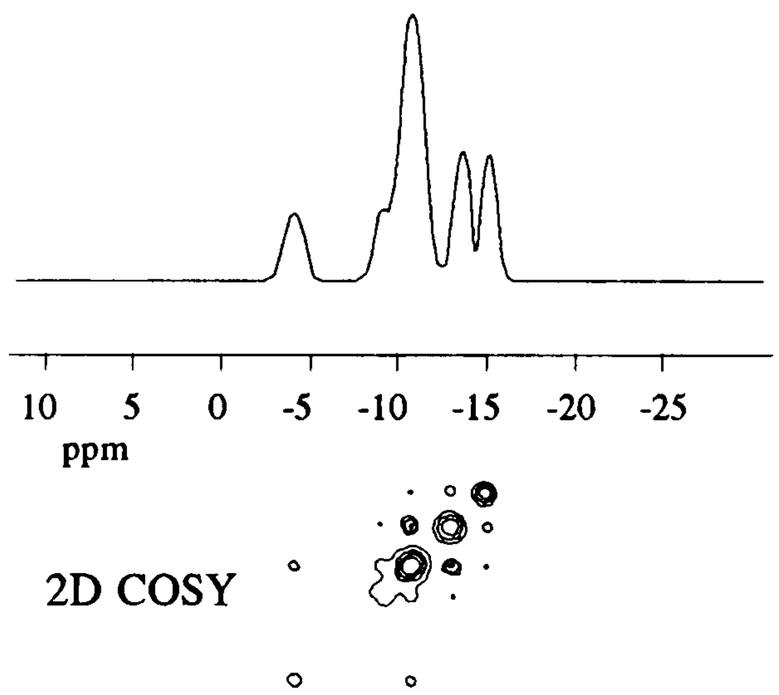
Mass spectrum (E.I.) A highest mass peak was observed at m/e 222 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 216 and 222.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.36-7.14	5	multiplet	aromatic C(a,b,c)-H
2.98	1	broad singlet	carboranyl C(f)-H
4.0-1.0	10	broad multiplet	carboranyl B-H

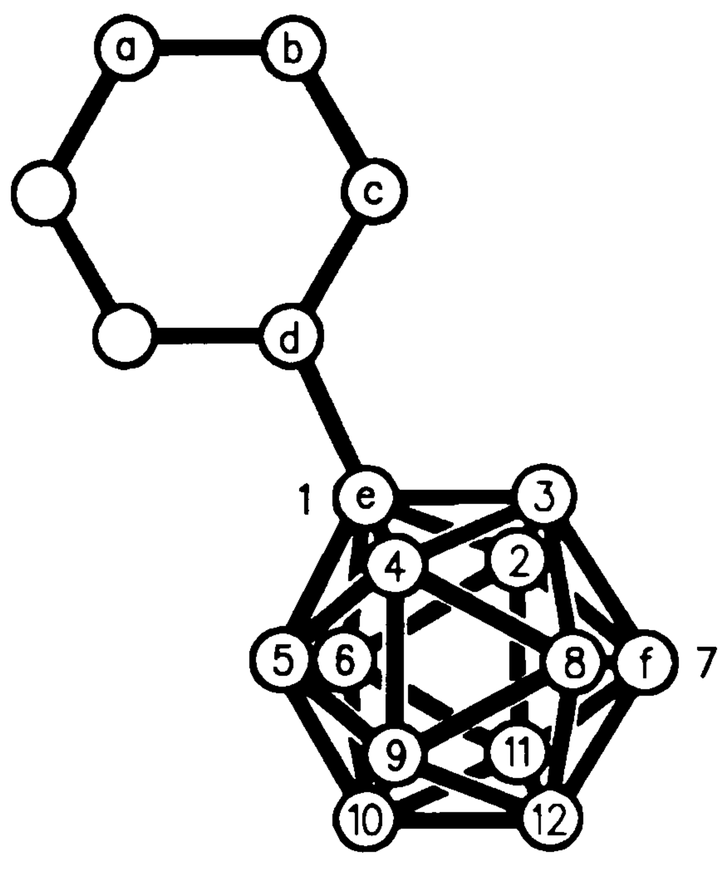
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-4.11	1	5
-9.04	1	12
-10.58	4	8,11,9,10
-13.56	2	4,6
-15.27	2	2,3



^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
135.11	d
128.64	a
128.30	b
127.77	c
78.33	e
55.05	f



CHAPTER 5

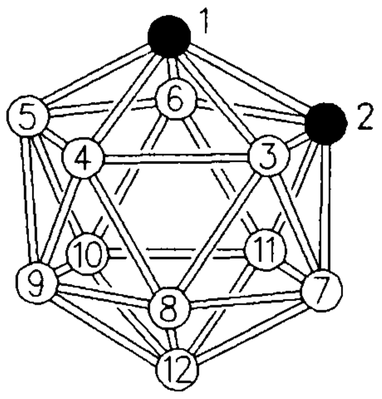
BORON-IODO CARBORANES

Boron-iodo carboranes are useful intermediates for boron-aryl carborane syntheses. This chapter describes the published preparations, preparation carried out, chemical properties and nuclear magnetic resonance study of boron-iodo carboranes.

BACKGROUND

Boron-iodo carboranes can be made by electrophilic iodination on the parent carborane at boron-hydrogen bonds. The direct attack of iodine on the carborane system has been shown in numerous studies to be highly stereospecific[1,2,3,4,5].

Reacting 1-phenyl- and 1-methyl-*ortho*-carborane with a half molar amount of iodine gave two boron-iodo-1-phenyl and two boron-iodo-1-methyl isomers respectively indicating attack at the 9- or 12- position of the *ortho*-carborane cage which was confirmed by X-ray structure of the isolated 12-iodo-1-phenyl-*ortho*-carborane isomer[5,6]. With iodine in excess, the second iodine atom occupies the vacant 9- or 12- position while the third enters 8- or 10- position with the fourth filling the vacant one of the latter positions[2,3]. Charge distribution calculations correlate well with the observed sequence of substitutions where the negative charge of the cage atoms decreases in order as shown below[7,8,9];



9,12 > 8,10 > > 4,5,7,11 > 3,6 > 1,2

Treatment of *ortho*-carborane with iodine in carbon tetrachloride over a catalyst, dry aluminium chloride or iron and iron chloride, at 80°C (preferred to 180°C without catalyst which gives a mixture of products[10]) gave mainly 9-iodo- and 9-iodo-12-chloro-*ortho*-carborane[11].

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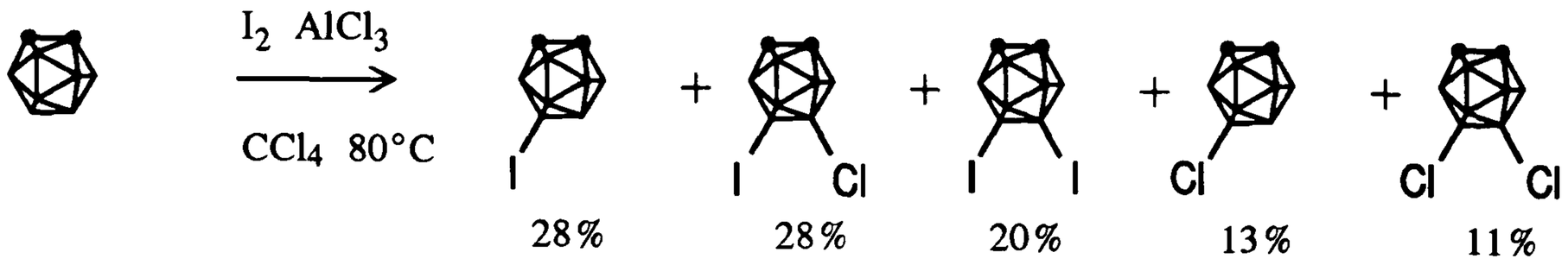
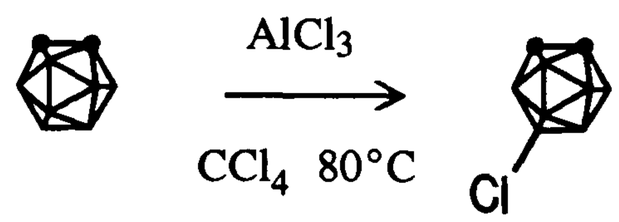
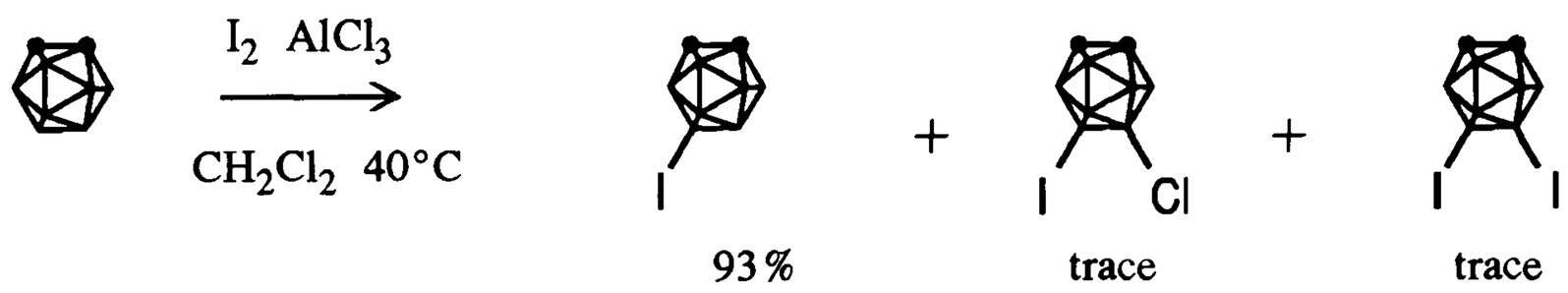
1. Zakharkin L.I. Kalinin V.N. *J. Gen. Chem. U.S.S.R.* 1966 **36** 2213
2. Stanko V.I.,Struchkov Yu.T. Klimova A.I. *Zh. Strukt. Khim.* 1966 **7** 629-630 (Russ) [CA65:16810e]
3. Zakharkin L.I. Kalinin V.N. *Dokl. Akad. Nauk. S.S.S.R.* 1966 **170** 92-95 (Russ) [CA66:46448t]
4. Zakharkin L.I. Kalinin V.N. Lozovskaya V.S. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1968 1683-1688
5. Stanko V.I. Struckhov Yu.T. Klimova A.I. Bryukhova L.V. Semin G.K. *J. Gen. Chem. U.S.S.R.* 1966 **36** 1703
6. Stanko V.I. Struckhov Yu.T. *J. Gen. Chem. U.S.S.R.* 1965 **35** 935
7. Potenza J.A. Lipscomb W.N. Vickers G.D Schroeder H. *J. Am. Chem. Soc.* 1966 **88** 628-629
8. Potenza J.A. Lipscomb W.N. *Inorg. Chem.* 1966 **5** 1471-1477
9. Beall H. Lipscomb W.N. *Inorg. Chem.* 1967 **6** 874-879
10. Zakharkin L.I. Stanko V.I. Klimova A.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1966 1882-1888
11. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1966 549-551



Aluminium chloride was found to be more regioselective[12] in electrophilic attack than the iron catalyst but the former catalyst, unlike the latter, chlorinates the carborane (again in the 9- position) with chlorinated solvents like carbon tetrachloride, chloroform and methylene dichloride[13,14].



After extensive trials, the best reagents and conditions for 9-iodo-*ortho*-carborane formation are *ortho*-carborane and iodine in methylene dichloride with dry powdered aluminium chloride at 40°C[4,13,15]. The 93% yield of 9-iodo-*ortho*-carborane product (this compound always contains a small amount of 8-iodo-*ortho*-carborane[4] which is inseparable from the main product) is accompanied by 9-chloro-12-iodo- and 9,12-diiodo-*ortho*-carboranes in trace amounts.



Aluminium chloride-catalysed iodination of 1-vinyl-[16], 1-methyl- and 1-phenyl-[17]*ortho*-carborane gives boron-iodo products where the vinyl, methyl and phenyl groups are unaffected.

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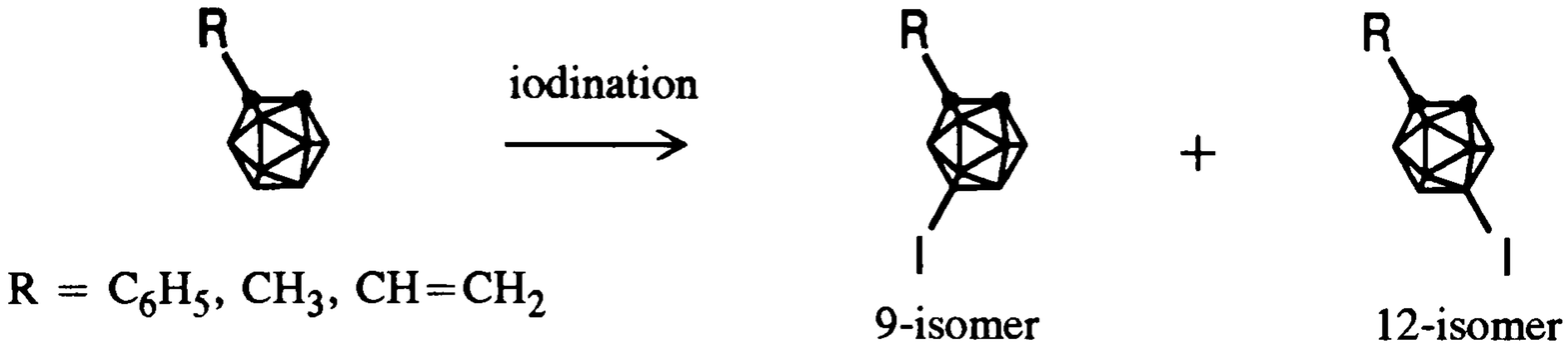
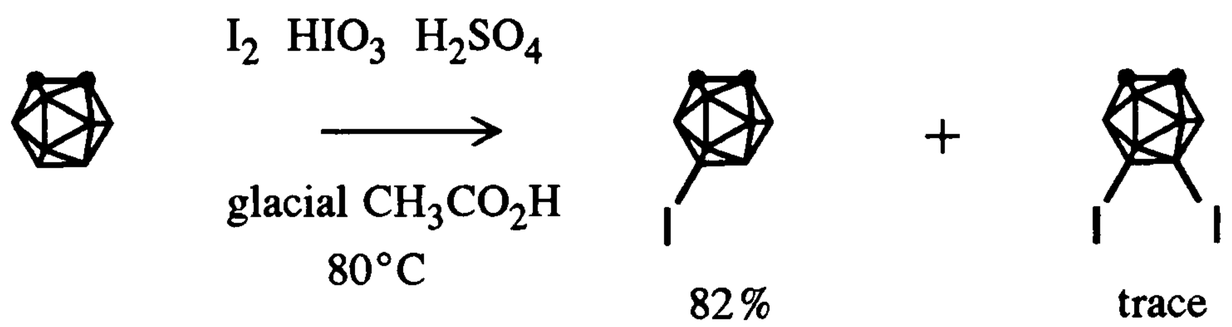
12. Stanko V.I. Klimova A.I. Klimova T.P. *J. Gen. Chem. U.S.S.R.* 1967 **37** 2123-2128
13. Andrews J.S. Zayas J. Jones M. *Inorg. Chem.* 1985 **24** 3715-3716
14. Zakharkin L.I. Okhlobystin O.Yu. Semin G.K. Babushkina T.A. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1965 1886
15. Zakharkin L.I. Ol'shevskaya V.A. Poroshina T.Yu. Balagurova E.V. *J. Gen. Chem. U.S.S.R.* 1987 **57** 1800-1803
16. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1967 908-910
17. Zakharkin L.I. Kalinin V.N. *J. Gen. Chem. U.S.S.R.* 1967 **37** 889-893



Electrophilic iodination of *ortho*-carborane can also be carried out using iodine, iodic acid and sulphuric acid on *ortho*-carborane with glacial acetic acid as solvent at 80°C[18]. Almost quantitative yields of 9-iodo-*ortho*-carborane (7% of 8-isomer) are obtained with no chlorine-containing side-products under moist conditions.



Another direct iodination method using iodine and [bis(trifluoroacetoxy)iodo]benzene, $(CF_3CO_2)_2IC_6H_5$, in carbon tetrachloride on *ortho*-carborane produces 9-iodo-*ortho*-carborane in 72% yield[19]. The latter compound can also be obtained from *ortho*-carborane via (9-*ortho*-carboranyl)thallium diiodide, 9-(1,2-$C_2B_{10}H_{11}$)TlI_2, or via the phenyl(9-*ortho*-carboranyl)iodonium tetrafluoroborate, [9-(1,2-$C_2B_{10}H_{11}$)IC_6H_5]$^+$[BF_4]$^-$[20,21].

8-iodo carborane derivatives can be made by iodinating decaborane before forming the carborane cage with a suitable alkyne[22,23]. At 120°C for 24 hours the decaborane is attacked by iodine at the 1- or 2- position to form two isomers of boron-iodo decaborane where the major isomer is 2-iododecaborane[24].

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18. Stanko V.I. Brattsev V.A. Vostrikova T.N. Danilova G.N. *J. Gen. Chem. U.S.S.R.* 1968 **38** 1300-1303

19. Merkushev E.B. Simakhina N.D. Grigorev M.G. *Izv. Akad. Nauk. S.S.S.R., Ser. Khim.* 1980 2649 (Russ) [CA94:103456y]

20. Demkina I.I. Grushin V.V. Vanchikov A.N. Tolstaya T.P. Orlinkov A.V. *J. Gen. Chem. U.S.S.R.* 1987 **57** 1199-1205

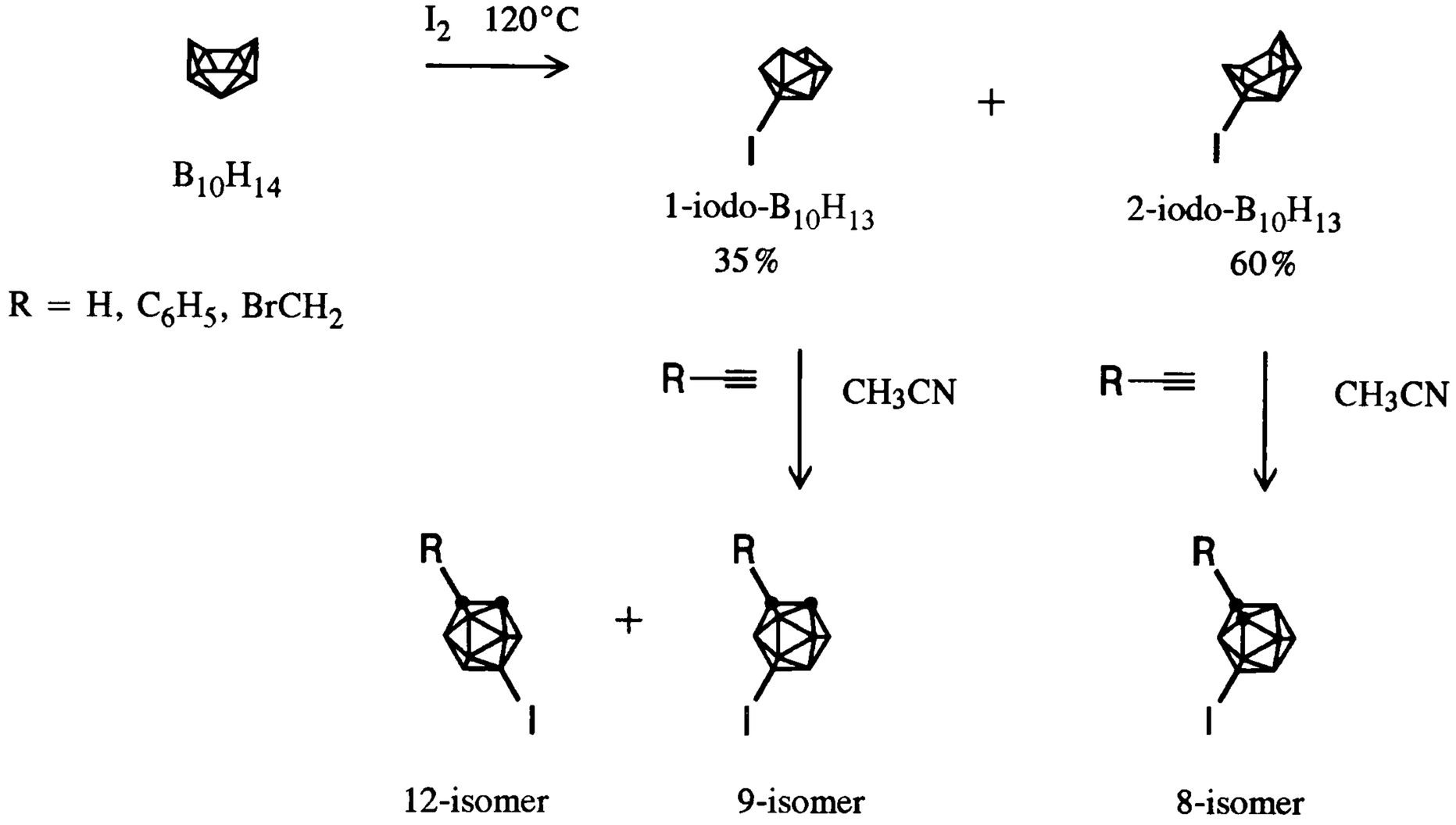
21. Grushin V.V. Shcherbina T.M. Tolstaya T.P. *J. Organometal. Chem.* 1985 **292** 105-117

22. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1966 566

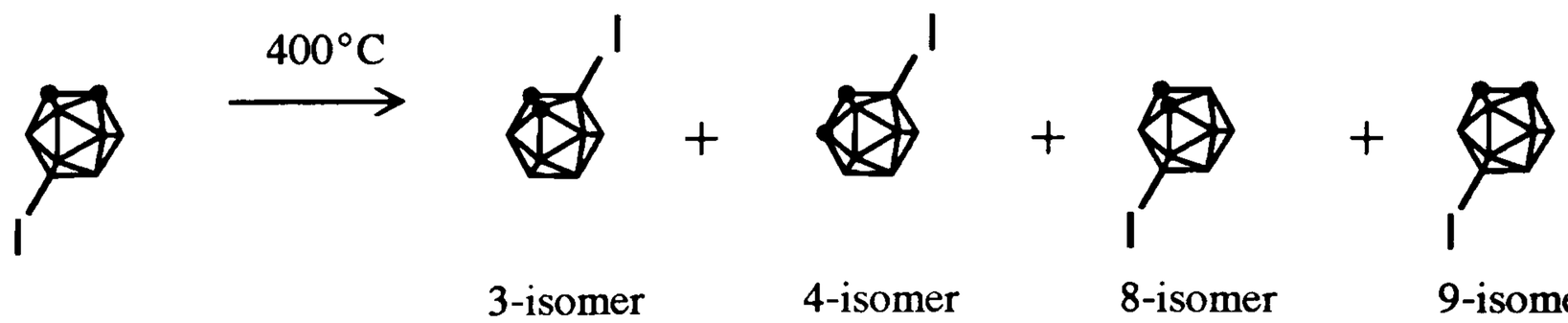
23. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1966 1946-1948

24. Sprecher R.F. Aufderheide B.E. Luther G.W. Carter J.C. *J. Amer. Chem. Soc.* 1973 **96** 4404-4410

The latter isomer and a suitable alkyne in refluxing acetonitrile form an 8-iodo-*ortho*-carborane derivative whereas 1-iododecaborane gives 9- and 12-iodo-*ortho*-carborane derivatives with a terminal alkyne.



3- and 4-iodo-*ortho*-carboranes are formed from thermal rearrangement of 9-iodo-*ortho*-carborane at 400°C[25]. It is thought that the iodine atom in boron-iodo carboranes exchanges with boron-linked hydrogen atoms intra- or intermolecularly at over 370°C[26].



9,12-diiodo-*ortho*-carborane is also obtained by the direct iodination methods with a 1 : 1 molar ratio of iodine and *ortho*-carborane[4,5,18,27].

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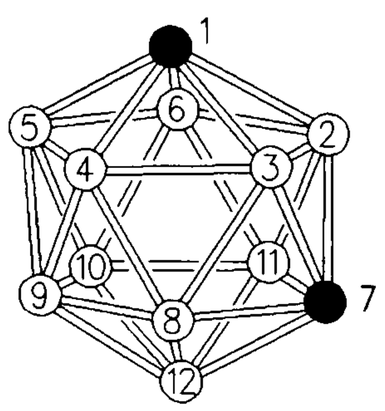
25. Zakharkin L.I. Kovredov A.I. Ol'shevskaya V.A. Vitt S.V. *J. Gen. Chem. U.S.S.R.* 1985 **55** 908-917
26. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1969 542-545
27. Zakharkin L.I. Kalinin V.N. *Dokl. Akad. Nauk. S.S.S.R.* 1966 **169** 590-593 (Russ) [CA65:15413a]

In the *meta*-carborane system, molecular orbital calculations have placed the highest negative charge on the 9- and 10- positions which are the only ones not adjacent to the positive carbon atoms[9,28]. The order of decreasing negative charge is;



9,10 > > 5,12 > 4,6,8,11 > > 2,3 > 1,7

Iodine actually attacks the 9- or 10- position of the *meta*-carborane and the second iodine if any occupies the vacant 9- or 10- position[1,2].

9-iodo-*meta*-carborane can be obtained from *meta*-carborane with the same direct methods[11,18,29] as for 9-iodo-*ortho*-carborane formation but the conditions required for completion are more severe as the rate of iodination ratio between *ortho* and *meta* is 11.5:1[1]. The negative charge on 9- and 12- boron positions of *ortho*-carborane is higher than on 9- and 10- boron positions of *meta*-carborane according to molecular orbital calculations as the positive carbon atoms in *meta* carborane are further apart giving a more even charge distribution throughout the cage compared to *ortho*-carborane[9,29].

A mixture of 4-, 5- and 9-iodo-*meta*-carboranes can be formed by thermal rearrangement and isomerization of 9-iodo-*ortho*-carborane at 560°C and 1mmHg[26].

28. Stanko V.I. Echeistova A.I. Astakhova I.S. Klimova A.I. Struckhov Yu.T. Syrkin Ya.K. *Zh. Strukt. Khim.* 1967 **8** 928-32 (Russ) [CA68:86720y]

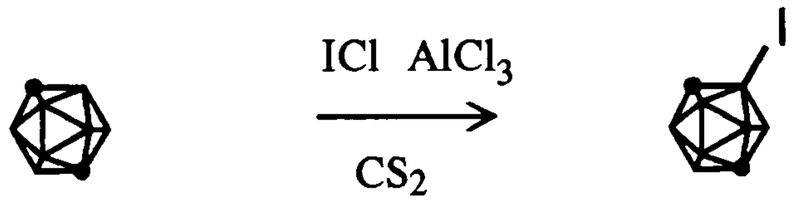
29. Stanko V.I. Gol'tyapin Yu.V. *J. Gen. Chem. U.S.S.R.* 1970 **40** 115-118

Para-carborane contains identical borons in its cage so only one isomer of boron-iodo-*para*-carborane can be formed. The order of decreasing rate of electrophilic iodination on parent carborane isomers, confirmed in competing iodination of a mixture of the three isomers, is[29,30];

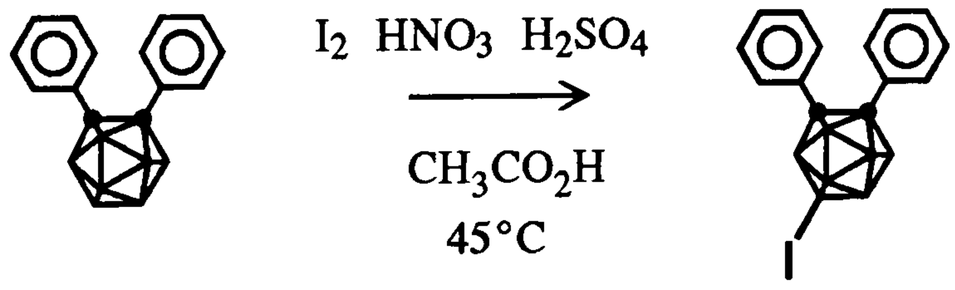
ortho > *meta* > > *para*

Molecular orbital calculations showed very low negative charges on the boron atoms of *para*-carborane with respect to the negative charges in the 9-position boron atoms of *ortho*- and *meta*-carborane which explains the low reactivity of the *para* isomer compared to *ortho* and *meta* isomers in electrophilic iodination.

2-iodo-*para*-carborane is made from iodine monochloride, a stronger iodinating agent than iodine, and *para*-carborane with aluminium chloride in carbon disulphide[29,30].



9-iodo-1,2-diphenyl-*ortho*-carborane is obtained from 1,2-diphenyl-*ortho*-carborane and iodine with a mixture of nitric and sulphuric acid in acetic acid at 45°C[31].



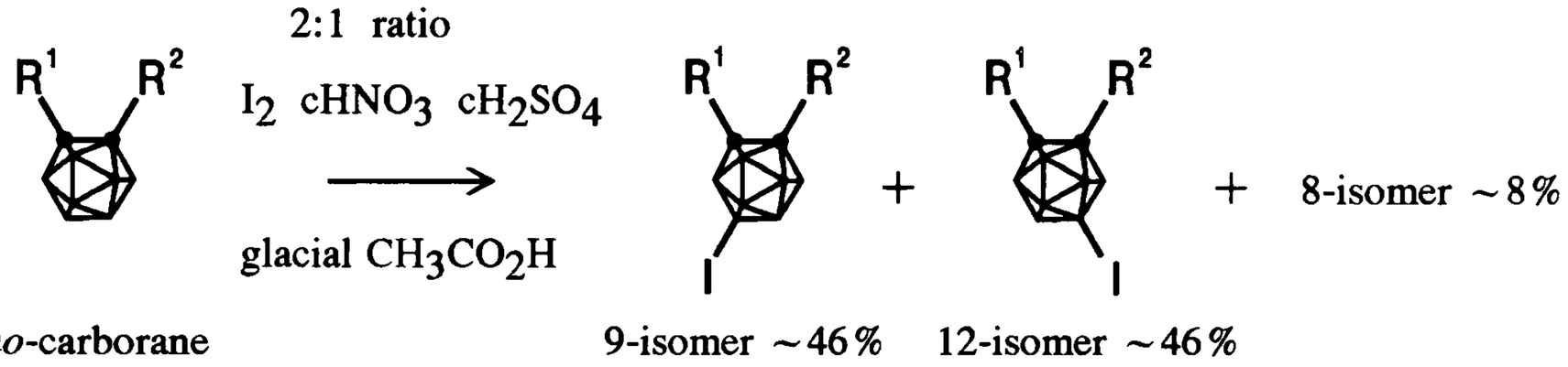
30. Stanko V.I. Gol'tyapin Yu.V. *J. Gen. Chem. U.S.S.R.* 1969 **39** 676

31. Vasil'eva V.P. Khalfina I.L. *Deposited Doc.* 1976 VINITI 2178-76 6 (Russ) [CA89:129573f]

PREPARATION OF BORON-IODO CARBORANES

The iodic acid method was chosen over aluminium chloride iodination as it eliminates both the need for dry conditions and any chlorine-containing side products. The method worked well on *ortho*-carborane where the mixture decolorized after 90 minutes (lit[18]. 45 mins.) and 86% yield of 9-iodo-*ortho*-carborane was obtained. The same method was attempted on 1-phenyl-*ortho*-carborane and after refluxing for 24 hours, the colour of the mixture remained and only starting material was recovered.

A simple modification of the iodic acid method by changing from iodic acid to nitric acid gave a good yield of boron-iodo-1-phenyl-*ortho*-carborane with the decolorization time of only 45 minutes. The nitric acid method was carried out on other carborane derivatives with success, the decolorization times are shown in the table below.



	R^1	R^2	ratio	temp.	acid	time
ortho	H	H	2:1	40°C	7ml	20min
ortho	CH_3	H	2:1	40°C	10ml	25min
ortho	CH_3	CH_3	2:1	40°C	15ml	30min
ortho	C_6H_5	H	2:1	80°C	15ml	45min
ortho	C_6H_5	C_6H_5	2:1	80°C	20ml	80min
ortho	$C_6H_4CH_3$	H	2:1	80°C	20ml	45min
ortho	H	H	1:1	80°C	25ml	60min
meta	H	H	2:1	80°C	20ml	45min
meta	H	H	1:1	80°C	30ml	120min

This table is based on 0.1 mole of carborane in 40 ml of glacial acetic acid,

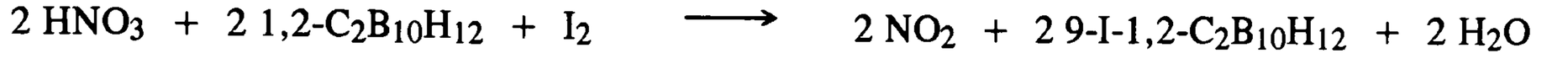
ratio = molecular ratio $R^1R^2C_2B_{10}H_{10} : I_2$,

temp. = temperature of solution,

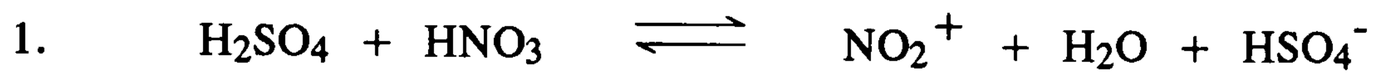
acid = mixture of 1:1 concentrated nitric : sulphuric acid,

time = time from start of reaction to decolorization.

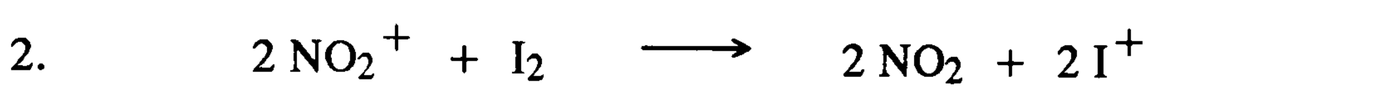
The decolorization period is not very accurate as the solution changes from purple to brown. The latter colour is due to brown nitrogen dioxide fumes[32] produced during the reaction. The probable equation of this reaction and its steps are;



$$2\,HNO_3 + 2\,1,2\text{-}C_2B_{10}H_{12} + I_2 \longrightarrow 2\,NO_2 + 2\,9\text{-}I\text{-}1,2\text{-}C_2B_{10}H_{12} + 2\,H_2O$$



1. $H_2SO_4 + HNO_3 \rightleftharpoons NO_2^+ + H_2O + HSO_4^-$



2. $2\,NO_2^+ + I_2 \longrightarrow 2\,NO_2 + 2\,I^+$

3. $I^+ + 1,2\text{-}C_2B_{10}H_{12} \longrightarrow 9\text{-}I\text{-}1,2\text{-}C_2B_{10}H_{12} + H^+$

The reaction may be radical as the second step could be;

2. $NO_2^+ + I_2 \longrightarrow NO_2 + I^+ + I^{\cdot}$

Gas chromatography and nuclear magnetic resonance studies show that all mono-iodo-*ortho*-carborane products contain equal amounts of 9- and 12- isomers with 7-11% of 8- isomer. Of the different 9- and 12- isomers produced only the 12-iodo-1-phenyl-*ortho*-carborane has been isolated by freak fractional crystallization which could not be repeated. Attempts by using preparative thin layer chromatography[33] have not been successful at isolating these 9- and 12- isomers.

The advantage of the nitric acid over the published iodic acid method is the faster reaction times for iodinating carboranes. The benefits of this new method over the aluminium chloride method are;

i) no essential dry conditions,

ii) faster decolorization times,

iii) no chlorine-containing side products.

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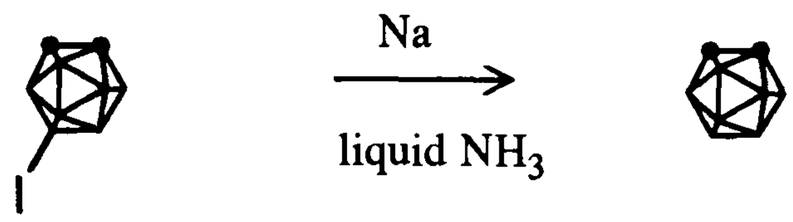
33. Zakharkin L.I. Kalinin V.N. *J. Gen. Chem. U.S.S.R.* 1967 **37** 1633-1636

PROPERTIES OF BORON-IODO CARBORANES

Unwanted boron-iodo carboranes can be reconverted into their parent carboranes by reducing the boron-iodine to a boron-hydrogen bond with sodium metal and liquid ammonia[34,35].



Boron-iodo carboranes can be converted into boron-chloro carboranes by substitution of the boron-iodine bond using copper (I) chloride[36,37].

Claims that 9-iodo-*ortho*-carborane undergoes isotopic exchange with radioactive sodium iodide-131 at room temperature[38,39,40] and that 9-iodo-*ortho*-carborane with copper metal and tetrahydrofuran form 9,9′-bis-*ortho*-carborane[41] could not be repeated in further investigations[37,39,42].

The formation of boron-aryl carboranes from boron-iodo carboranes is described in Chapter 5. Boron-alkyl, -alkynyl and -alkenyl carboranes can be formed by the same route[27,43,44,45].

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37. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1967 2460-2462

38. Stanko V.I. Gol'tyapin Yu.V. Volkov A.F. *J. Gen. Chem. U.S.S.R.* 1967 **37** 485

39. Stanko V.I. Iroshnikova N.G. *J. Gen. Chem. U.S.S.R.* 1970 **40** 281-284

40. Stanko V.I. Iroshnikova N.G. *Nov. Melody Poluch. Radioaktiv. Prep., Sb. Dokl. Simp.* 1969(Publ.1970) 486-510 (Russ) [CA74:125760g]

41. Stanko V.I. Gol'tyapin Yu.V. Brattsev V.A. *J. Gen. Chem. U.S.S.R.* 1967 37 2247

42. Lane R.A. "Studies on the synthesis and derivative chemistry of icosahedral carboranes" Ph.D.Thesis Durham 1982 p152.

43. Zakharkin L.I. Kovredov A.I. Ol'shevskaya V.A. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1985 809-812

44. Zakharkin L.I. Kovredov A.I. Ol'shevskaya V.A. Shaugumbekova Zh.S. *J. Organometal. Chem.* 1982 **226** 217-222

45. Kovredov A.I. Shaugumbekova Zh.S. Petrovskii P.V. Zakharkin L.I. *J. Gen. Chem. U.S.S.R.* 1989 **59** 537-540

N.M.R. STUDY OF BORON-IODO CARBORANES

^{1}H, ^{11}B {^{1}H decoupled} and ^{13}C {^{1}H decoupled} n.m.r. spectra of all boron-iodo carboranes, including isomer mixtures, produced were obtained using $CDCl_3$ as solvent. ^{11}B peak assignments of boron-iodo carboranes were determined with the aid of ^{11}B n.m.r. spectroscopy, ^{11}B 2D COSY n.m.r. or peak shape analysis. The antipodal effect of the iodine atom on the ^{1}H, ^{11}B and ^{13}C chemical shifts is strong[46,47] and n.m.r. data for these derivatives could give insight into the antipodal effect mechanism. Chemical shift peaks and assignments of ^{11}B n.m.r. spectra of carborane derivatives are difficult to predict so calculations loosely based on the geometrical rules[48] for ^{11}B n.m.r. chemical shifts were compared with observed ^{11}B n.m.r. data for 9-iodo-*ortho*-carborane derivatives obtained in this study.

The difference between known ^{11}B and ^{13}C chemical shift values of *ortho*-carborane and 9-iodo-*ortho*-carborane was used to predict the shifts of the 9-iodo-*ortho*-carborane derivatives from those of the corresponding substituted carborane. An example is shown below (values in ppm);

	position	$1,2\text{-}C_2B_{10}H_{12}$	$9\text{-}I\text{-}1,2\text{-}C_2B_{10}H_{11}$	Difference
^{11}B	3,6	-16.07	-16.11	-0.04
	4,5	-15.00	-14.65	+0.35
	7,11	-15.00	-14.65	+0.35
	8,10	-10.60	-8.95	+1.65
	9	-3.80	-18.01	-14.21
	12	-3.80	-2.39	+1.41
^{13}C	1	54.46	54.90	+0.44
	2	54.46	50.74	-3.72

46. Zakharkin L.I. Kalinin V.N. Kozlova V.S. Antonovich V.A. *J. Gen. Chem. U.S.S.R.* 1973 **43** 844-847

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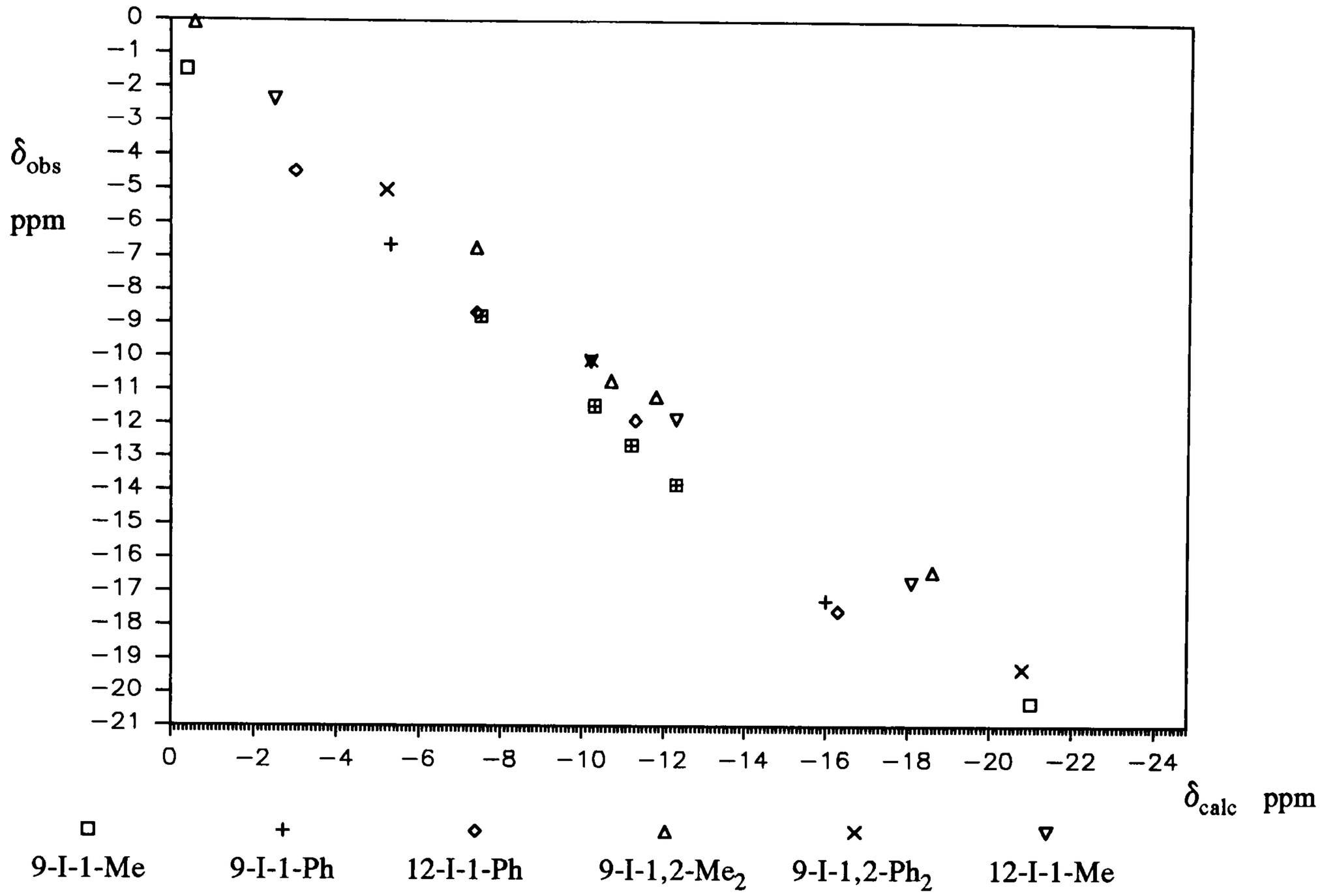
48. Texidor F. Vinas C. Rudolph R.W. *Inorg. Chem.* 1986 **25** 3339-3345

Add the difference in values to 1-methyl-*ortho*-carborane chemical shift values to obtain the calculated chemical shift values of 9-iodo-1-methyl-*ortho*-carborane (measured from a mixture of 9- and 12-iodo-1-methyl-ortho-carborane isomers);

position		1-Me-1,2-$C_2B_{10}H_{12}$	Calculated	Actual
^{11}B	3,6	-11.17	-11.21	-12.61
	4,5	-10.64	-10.29	-11.44
	7,11	-12.68	-12.33	-13.91
	8,10	-9.17	-7.52	-8.76
	9	-1.80	-16.01	-17.25
	12	-6.75	-5.34	-6.64
^{13}C	1	71.50	71.94	71.14
	2	62.16	58.44	57.87

By comparing the predicted chemical shift values and assignments with the actual values and assignments the calculations seem to agree very well with, in the boron resonances, an almost constant error of 1.1 to 1.6 ppm to lower field.

Calculations of the ^{11}B and ^{13}C chemical shifts of other 9-iodo-*ortho*-carborane derivatives were compared with the actual chemical shifts and found to correlate very well with the actual values (graph overleaf) which implies that the effect on the cage chemical shifts of iodine substituted at the 9- position of any *ortho*-carborane derivative is similar (non-equivalent 9- and 12- isomers of boron-iodo carboranes are measured as a mixture).



Graph showing correlation between observed ^{11}B chemical shifts, δ_{obs}, and calculated ^{11}B chemical shifts, δ_{calc}, in boron-iodo-*ortho*-carborane derivatives.

The correlation may also apply to other substituents for example the hydroxy group at the 9- position of *ortho*-carborane gave good predictions based on the difference in shifts of *ortho*-carborane and 9-hydroxy-*ortho*-carborane for 9-hydroxy-1,2-dimethyl-*ortho*-carborane.

	position	1,2-$C_2B_{10}H_{12}$	9-HO-1,2-$C_2B_{10}H_{11}$	Difference
^{11}B	3,6	-16.07	-16.92	-0.85
	4,5	-15.00	-15.12	-0.12
	7,11	-15.00	-16.30	-1.30
	8,10	-10.60	-10.00	+0.60
	9	-3.80	15.23	+19.03
	12	-3.80	-3.46	+0.34
^{13}C	1	54.46	49.06	-5.40
	2	54.46	37.01	-17.45

For 9-hydroxy-1,2-dimethyl-*ortho*-carborane

position		1,2-Me_2-1,2-$C_2B_{10}H_{12}$	Calculated	Actual
^{11}B	3,6	-9.61	-10.46	-9.48
	4,5	-10.92	-11.04	-9.48
	7,11	-10.92	-12.22	-10.99
	8,10	-11.16	-10.56	-9.48
	9	-6.61	+13.42	+15.49
	12	-6.61	-6.27	-5.24
^{13}C	1	73.37	67.97	68.13
	2	73.37	55.92	55.80

Calculations on the cage chemical shifts could be used to predict the ^{11}B and ^{13}C chemical shifts and assignments of a carborane derivative if experimental n.m.r. data of similar derivatives are known. Changes on the cage chemical shifts caused by three different substituents at the 9- position of *ortho*-carborane are shown below indicating the different effects each substituent has on the chemical shifts which could give insight into the antipodal effect mechanism.

position		I-	HO-	$C_6H_5OC_6H_4$-
^{11}B	3,6	-0.04	-0.85	+0.60
	4,5	+0.35	-0.12	+0.53
	7,11	+0.35	-1.30	+0.53
	8,10	+1.65	+0.60	+1.64
	9	-14.21	+19.03	+11.09
	12	+1.41	+0.34	+1.31
^{13}C	1	+0.44	-5.40	-1.32
	2	-3.72	-17.45	-5.79

CONCLUSIONS AND FUTURE WORK

A more efficient iodination of carboranes was found and twelve boron-iodo carboranes were conveniently obtained as a result although the possible 9- and 12-isomers obtained could not be separated. These carboranes are important in boron-aryl, -alkyl, -alkenyl and -alkynyl carborane syntheses. Nuclear magnetic resonance data of these boron-iodo carboranes were collected and calculations showed that iodine bonded to the 9- position gave similar effects on cage ^{11}B and ^{13}C chemical shift values in all 9-iodo-*ortho*-carborane derivatives. It has been shown that the ^{11}B chemical shift values of a carborane derivative could be predicted from known ^{11}B n.m.r. data of other carborane derivatives and the differences in the chemical shift values caused by different substituents could be investigated to probe the antipodal effect mechanism.

EXPERIMENTAL SECTION

The boron-iodo carboranes in this study were obtained by the iodic acid method, A, or the nitric acid method, B, or both. These methods are described in the 9-iodo-*ortho*-carborane section overleaf which are used in preparations of other boron-iodo carboranes.

9-iodo-1,2-dicarba-*closo*-dodecaborane

METHOD A

2.88g (20 mmoles) *ortho*-carborane was dissolved in 15ml glacial acetic acid with 2ml of 50% sulphuric acid, and 2.03g (8 mmoles) sublimed iodine and 0.70g (4 mmoles) iodic acid were added. The solution was heated at 90°C until the colour changed (90 minutes), cooled and poured into 300ml of distilled water. The precipitate was filtered off, washed with water and vacuum sublimed. The sublimate was recrystallized from hexane to give 4.64g (80%) of 9-iodo-*ortho*-carborane. Gas chromatography of the product in diethyl ether showed two peaks at 19.6 and 19.9 minutes with the area ratio 5 : 95 corresponding to 8- and 9-isomer peaks respectively. These isomers cannot be separated by preparative thin layer chromatography.

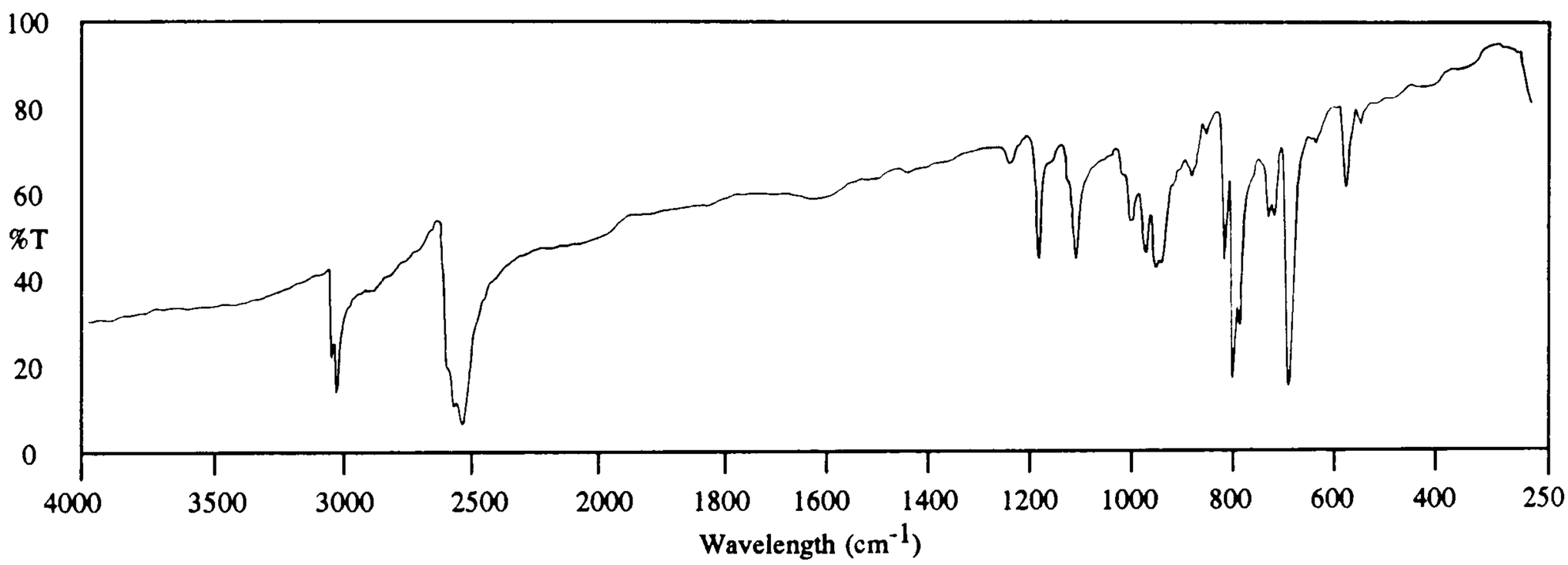
METHOD B

1.44g (10 mmoles) *ortho*-carborane and 1.27g (5 mmoles) iodine were dissolved in 40ml of glacial acetic acid with stirring at 40°C. 7ml of a mixture of 1:1 volume ratio concentrated nitric acid: concentrated sulphuric acid was added very slowly to the mixture, at the rate of 1ml per minute. A brown vapour was observed above the solution and within 20 minutes the solution became pale brown and then decolorized. The colourless solution was poured into a beaker of 300ml distilled water. The resulting white precipitate was filtered off, washed with distilled water, dissolved in diethyl ether and dried over anhydrous magnesium sulphate. The magnesium sulphate was filtered off and the ether removed using the rotary evaporator leaving an off-white residue which was recrystallized from hexane to give 2.40g (89%) of 9-iodo-*ortho*-carborane (5-7% of product is 8-isomer by g.c.).

Melting point = 123-123.5°C (lit[16]. = 123-124°C)

Analysis Found: C,8.9; H,4.1. $C_2H_{11}B_{10}I$ requires C,8.9; H,4.1.

Infrared (KBr disc; cm^{-1}) 3062(s), 3043(s), 2637(s), 2609(s), 2579(s), 1258(w), 1203(m), 1136(m), 1079(w), 1044(w), 1027(w), 999(m), 982(m), 971(m), 952(w), 940(w), 919(w), 915(w), 889(w), 851(m), 832(s), 821(s), 778(w), 764(w), 757(w), 726(s), 691(w), 679(w), 618(w).



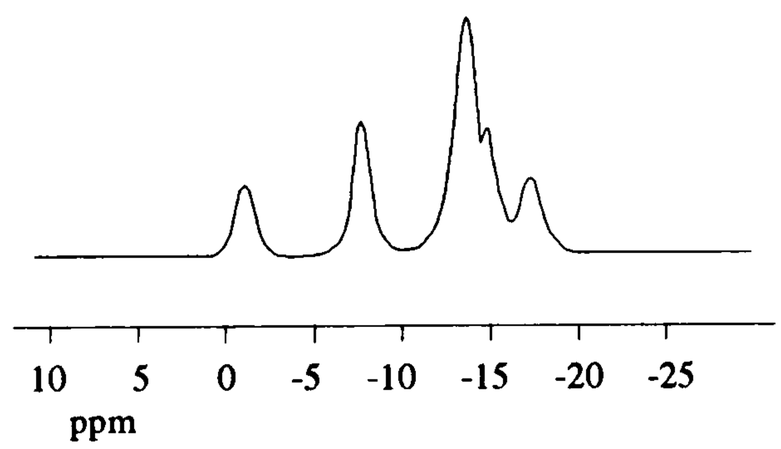
Mass spectrum (E.I.) A highest mass peak was observed at m/e 272 corresponding to the species $^{12}C_2{}^{1}H_{11}{}^{11}B_{10}{}^{127}I$, accompanied by the usual carborane isotope distribution pattern between m/e 266 and 272. A group of peaks were also observed between m/e 139-145 corresponding with $C_2H_{11}B_{10}$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

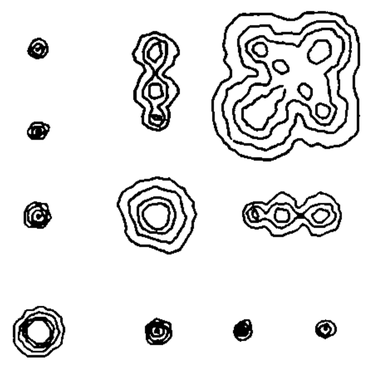
δ_{ppm}	intensity	type of peak	position of proton
4.0-0.7	10	broad multiplet	carboranyl B-H
3.88	1	broad singlet	carboranyl C(b)-H
3.68	1	broad singlet	carboranyl C(a)-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-2.39	1	12
-8.95	2	8,10
-14.65	4	4,5,7,11
-16.11	2	3,6
-18.01	1	9

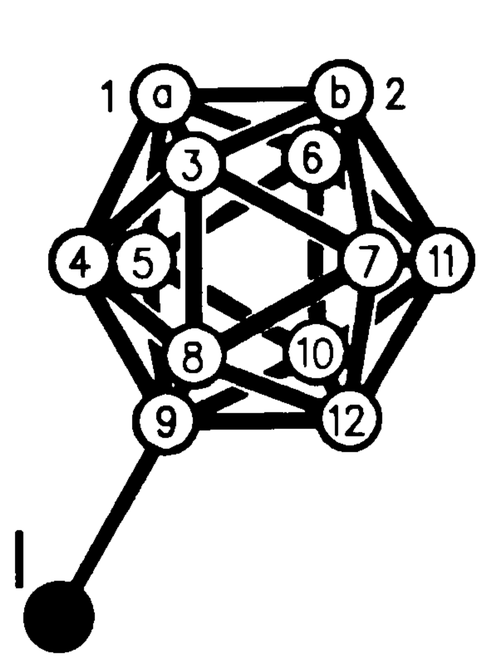


2D COSY

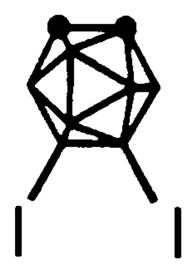


^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
54.90	a
50.74	b



9,12-diiodo-1,2-dicarba-*closo*-dodecaborane

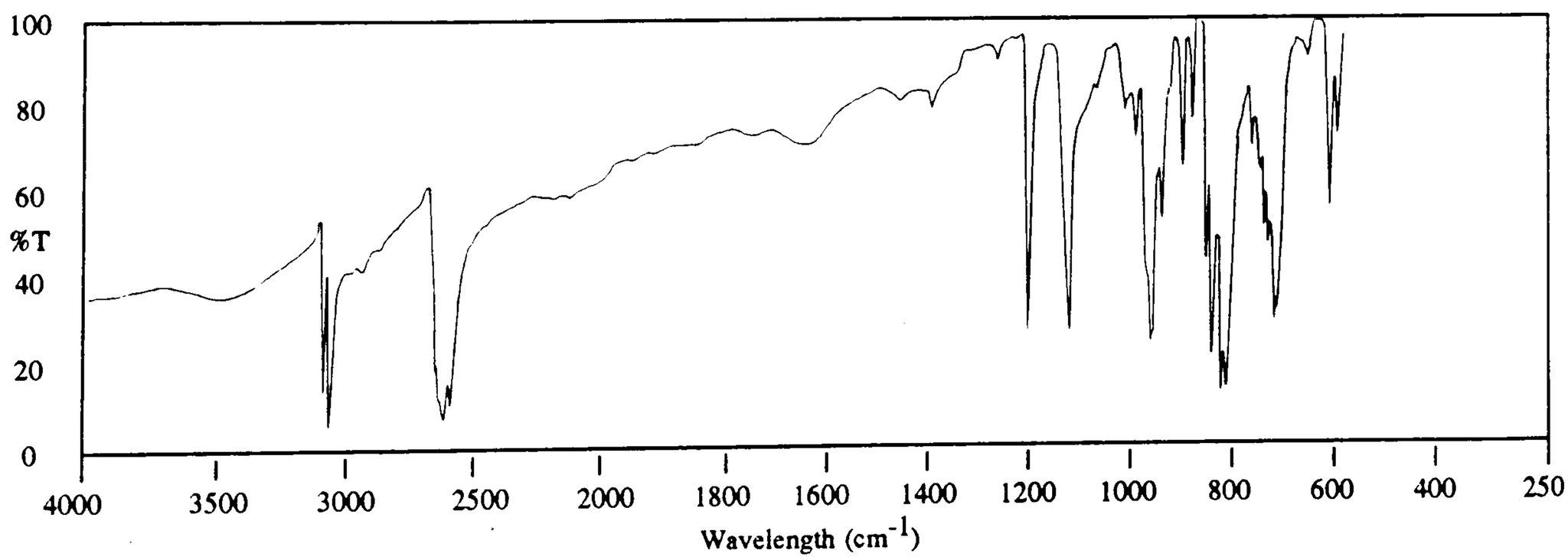


By method B, 1.44g (0.01 moles) *ortho*-carborane, 2.54g (0.01 moles) sublimed iodine and 25ml of nitric acid / sulphuric acid mixture in 40ml glacial acetic acid at 80°C for one hour gave 3.25g (82%) of 9,12-diiodo-*ortho*-carborane. Gas chromatography gave two peaks at 28.0 and 28.5 minutes with area ratio of 13 : 87 corresponding to 8,9- and 9,12- isomers respectively.

Melting point = 190-191°C (lit[16]. = 193-194°C)

Analysis Found: C,6.4; H,2.6. $C_2H_{10}B_{10}I_2$ requires C,6.1; H,2.5.

Infrared (KBr disc; cm^{-1}) 3066(s), 3041(s), 2965(w), 2930(w), 2854(w), 2648(s), 2636(s), 2622(s), 2616(s), 2588(s), 2155(w), 1391(w), 1268(w), 1210(s), 1137(s), 1082(w), 1026(w), 1020(w), 1003(w), 980(m), 977(s), 972(s), 952(m), 943(w), 922(w), 914(m), 898(w), 869(m), 857(s), 838(s), 827(s), 807(w), 781(w), 765(w), 757(m), 748(m), 734(s), 730(s), 720(w), 677(w), 672(w), 632(m), 618(w).



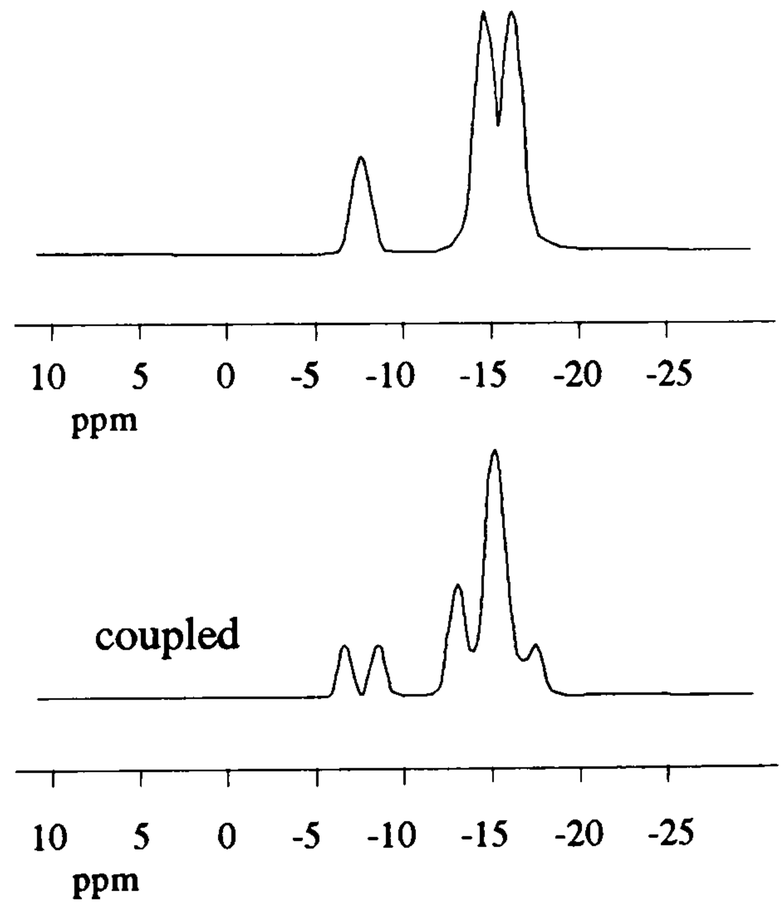
Mass spectrum (E.I.) A highest mass peak was observed at m/e 398 corresponding to the species $^{12}C_2{}^{1}H_{10}{}^{11}B_{10}{}^{127}I_2$, accompanied by the usual carborane isotope distribution pattern between m/e 392 and 398. Peaks present between m/e 265 and 271 were from $C_2B_{10}H_{10}I$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
4.0-1.0	8	broad multiplet	carboranyl B-H
4.00	2	broad singlet	carboranyl C-H

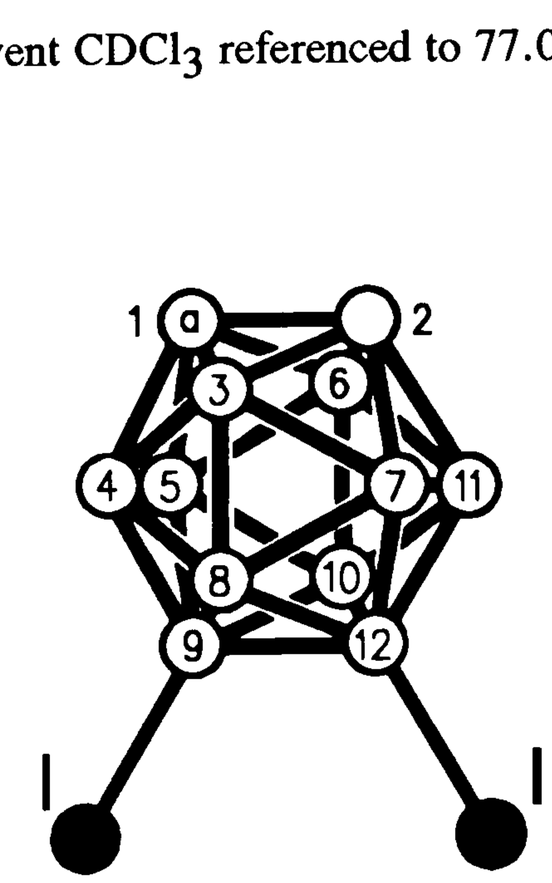
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-7.55	2	8,10
-14.92	4	4,5,7,11
-16.28	4	3,6,9,12



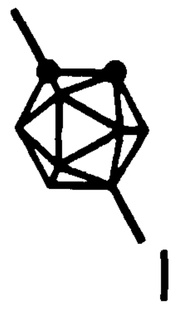
^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
52.23	a



Iodination of 1-methyl-1,2-dicarba-*closo*-dodecaborane

9- isomer

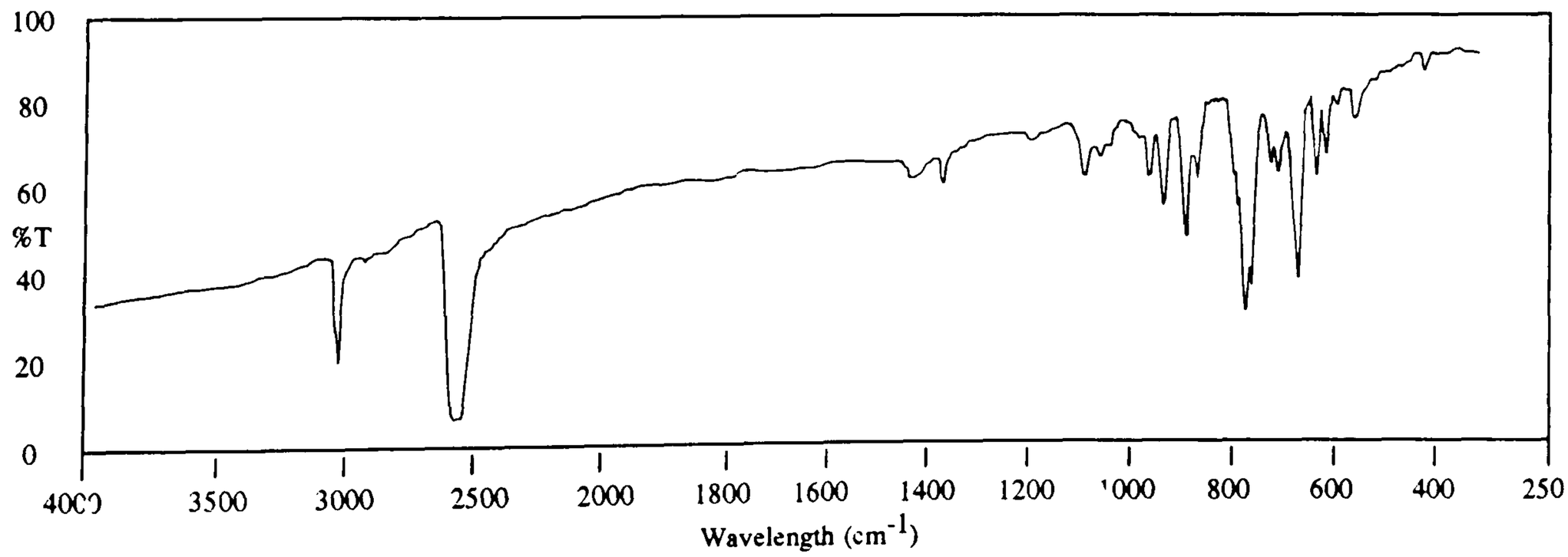


12- isomer

Using method B, 1.58g (10 mmoles) 1-methyl-*ortho*-carborane, 1.27g (5 mmoles) sublimed iodine and 10ml of nitric acid / sulphuric acid mixture in 40ml glacial acetic acid at 80°C for one hour gave 2.47g (87%) of a low melting solid identified as a mixture of 9- and 12-iodo-1-methyl-*ortho*-carborane isomers by gas chromatography: three peaks were observed probably corresponding to 8-isomer (19.2 minutes, 7%), 9- isomer (19.8, 48%) and 12- isomer (19.9, 46%). These isomers could not be separated by means of column chromatography or fractional crystallization. The ^{1}H, ^{11}B and ^{13}C N.M.R. peaks are assigned to 9- and 12- isomers in the mixture by comparison with other iodinated products described in this chapter.

Analysis Found: C,9.4; H,3.3. $C_3H_{13}B_{10}I$ requires C,9.4; H,3.4.

Infrared (KBr disc; cm^{-1}) 3055(s), 2959(m), 2947(m), 2934(m), 2877(w), 2865(w), 2638(s), 2600(s), 2561(s), 1856(w), 1567(w), 1524(w), 1485(m), 1451(m), 1391(m), 1348(w), 1229(w), 1210(w), 1129(m), 1109(m), 1097(m), 1082(w), 1060(w), 1033(w), 1016(m), 1007(m), 1005(m), 978(m), 937(m), 920(w), 885(w), 838(s), 828(s), 823(s), 813(s), 806(m), 780(m), 767(m), 742(m), 730(s), 723(s), 692(w), 674(w), 655(w), 620(w), 490(w), 470(w), 457(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 286 corresponding to the species $^{12}C_3{}^{1}H_{13}{}^{11}B_{10}{}^{127}I$, accompanied by the usual carborane isotope distribution pattern between m/e 280 and 286. Other peaks observed between m/e 151 and 157 were identified as $C_3H_{13}B_{10}$.

9-iodo-1-methyl-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

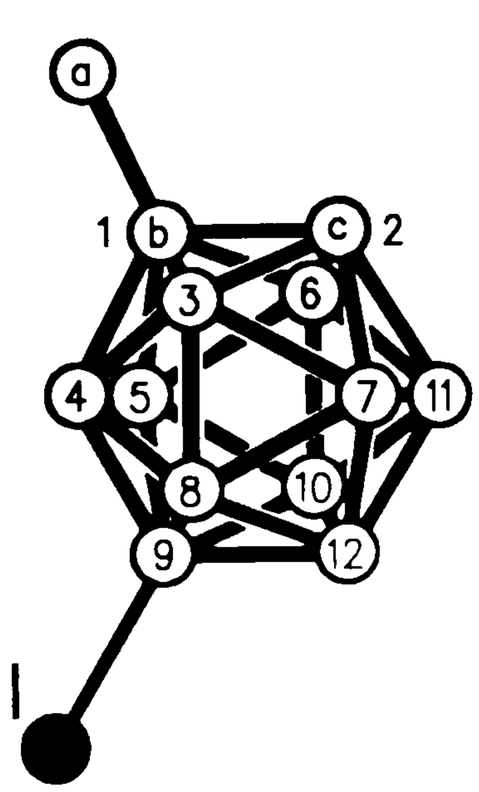
δ_{ppm}	intensity	type of peak	position of proton
3.70	1	broad singlet	carboranyl C(c)-H
2.17	3	singlet	methyl C(a)-H
4.0-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-6.64	1	12
-8.76	2	8,10
-11.44	2	4,5
-12.61	2	3,6
-13.79	2	7,11
-17.25	1	9

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
71.14	b
57.87	c
25.55	a



12-iodo-1-methyl-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

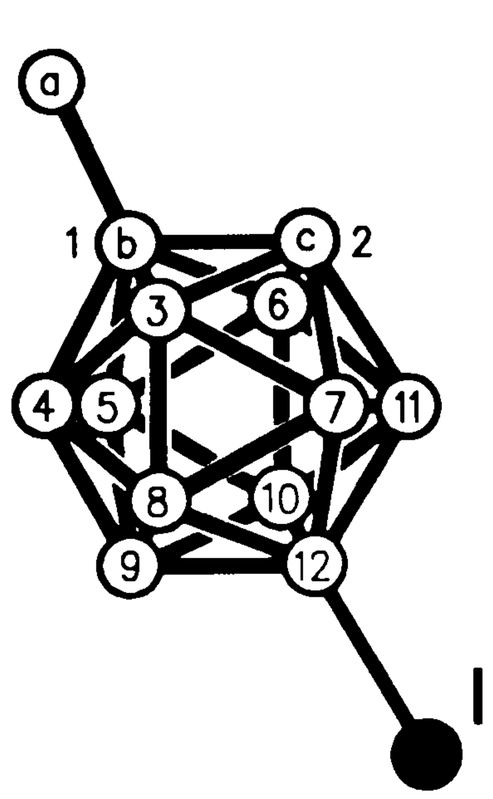
δ_{ppm}	intensity	type of peak	position of proton
3.89	1	broad singlet	carboranyl C(c)-H
2.06	3	singlet	methyl C(a)-H
4.0-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

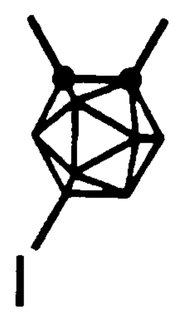
δ_{ppm}	intensity	position of boron
-1.48	1	9
-8.76	2	8,10
-11.44	2	4,5
-12.61	2	3,6
-13.79	2	7,11
-20.31	1	12

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
66.92	b
62.32	c
25.55	a



9-iodo-1,2-dimethyl-1,2-dicarba-*closo*-dodecaborane



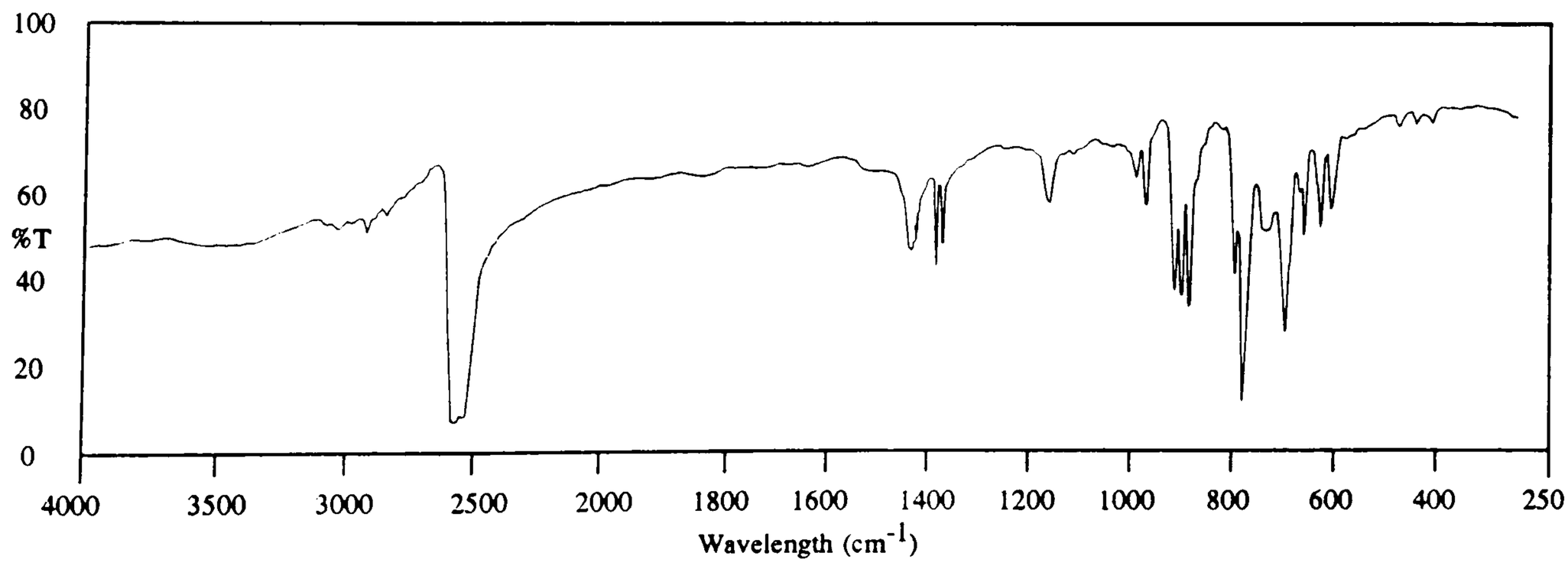
By method A, 1.72g (10 mmoles) 1,2-dimethyl-*ortho*-carborane, 1.02g (4 mmoles) sublimed iodine, 0.35g (2 mmoles) iodic acid and 1.5ml of 50% sulphuric acid in 10ml glacial acetic acid at 80°C for two hours gave 2.47g (83%) of 9-iodo-1,2-dimethyl-*ortho*-carborane.

With method B, 1.72g (10 mmoles) 1,2-dimethyl-*ortho*-carborane, 1.27g (5 mmoles) sublimed iodine and 15ml of nitric acid / sulphuric acid mixture in 40ml glacial acetic acid at 40°C for 25 minutes gave 2.44g (82%) of 9-iodo-1,2-dimethyl-*ortho*-carborane.

Melting point = 133-134°C (lit[49]. = 129-130°C)

Analysis Found: C,15.7; H,5.1. $C_4H_{15}B_{10}I$ requires C,16.1; H,5.0.

Infrared (KBr disc; cm^{-1}) 3042(w), 2992(w), 2935(w), 2902(w), 2861(w), 2600(s), 2587(s), 2576(s), 2560(s), 1442(m), 1395(m), 1383(m), 1182(m), 1140(w), 1019(w), 1000(m), 945(m), 931(m), 918(m), 902(w), 889(w), 831(m), 816(s), 780(m), 772(m), 763(m), 749(m), 732(s), 728(m), 708(w), 699(m), 667(m), 646(m), 518(w), 486(w), 455(w).



49. Zakharkin L.I. Kalinin V.N. Snyakin A.P. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1968 194-196

Mass spectrum (E.I.) A highest mass peak was observed at m/e 300 corresponding to the species $^{12}C_4{}^{1}H_{15}{}^{11}B_{10}{}^{127}I$, accompanied by the usual carborane isotope distribution pattern between m/e 294 and 300. Peaks between m/e 167 and 173 were observed and identified as $C_4H_{15}B_{10}$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

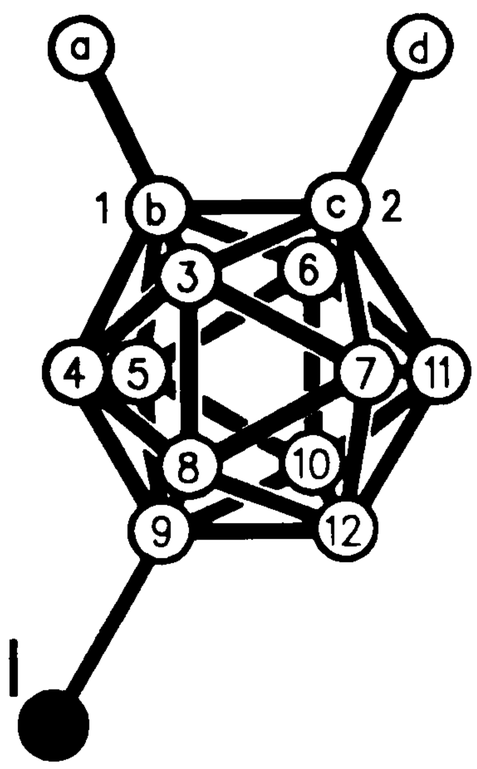
δ_{ppm}	intensity	type of peak	position of proton
2.06	3	singlet	methyl C(d)-H
1.91	3	singlet	methyl C(a)-H
4.1-0.9	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

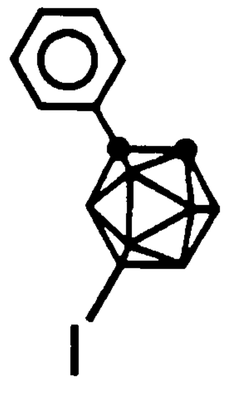
δ_{ppm}	intensity	position of boron
-5.03	1	12
-10.09	8	3,6,4,5,7,11,8,10
-19.29	1	9

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

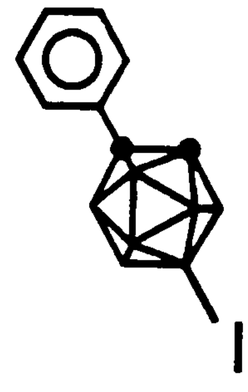
δ_{ppm}	position of carbon
74.30	b
69.90	c
23.07	a,d



Iodination of 1-phenyl-1,2-dicarba-*closo*-dodecaborane



9- isomer

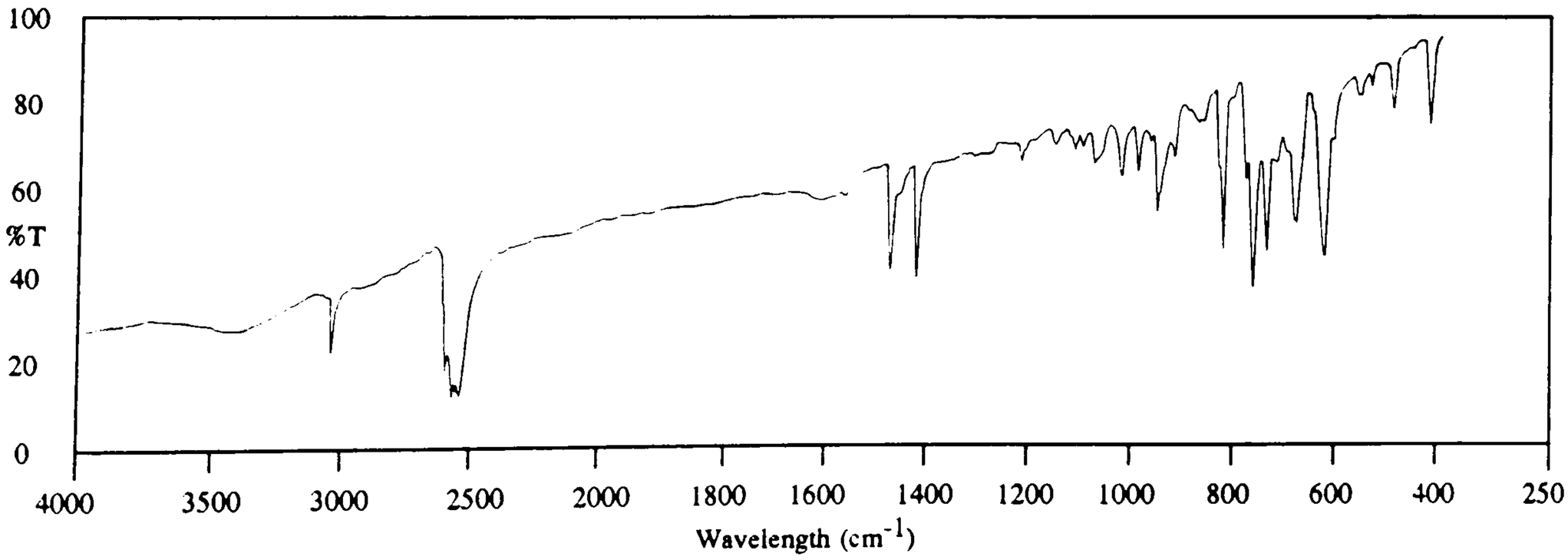


12- isomer

Using method B, 2.20g (10 mmoles) 1-phenyl-*ortho*-carborane, 1.27g (5 mmoles) sublimed iodine and 15ml of nitric acid / sulphuric acid mixture in 40ml of glacial acetic acid at 80°C for 45 minutes gave 3.18g (92%) of a product containing 9- and 12-iodo-1-phenyl-*ortho*-carborane isomers. Gas chromatography, using diethyl ether as solvent for injection, showed three peaks at 34.7, 35.8 and 36.3 minutes with area ratio 11 : 44 : 45 for 8-, 9- and 12- isomers respectively. A freak fractional crystallization in hexane which could not be repeated gave 0.12g of pure 12-iodo-1-phenyl-*ortho*-carborane. (Gas chromatography gave one peak at 36.4 minutes.)

Analysis Found: C,27.7; H,4.4. $C_8H_{15}B_{10}I$ requires C,27.8; H,4.3.

Infrared (KBr disc; cm^{-1}) 3065(w), 3058(w), 3043(m), 2641(m), 2632(s), 2607(s), 2596(s), 2580(s), 1589(w), 1578(w), 1492(m), 1479(w), 1445(m), 1382(w), 1336(w), 1317(w), 1258(m), 1236(w), 1191(w), 1162(w), 1156(w), 1140(w), 1118(m), 1108(m), 1081(m), 1068(m), 1037(m), 1013(w), 1000(m), 971(w), 942(w), 927(w), 913(w), 882(m), 878(s), 858(w), 832(m), 821(s), 796(s), 780(m), 776(m), 757(m), 740(s), 687(s), 670(m), 618(w), 612(w), 592(w), 554(w), 482(m).



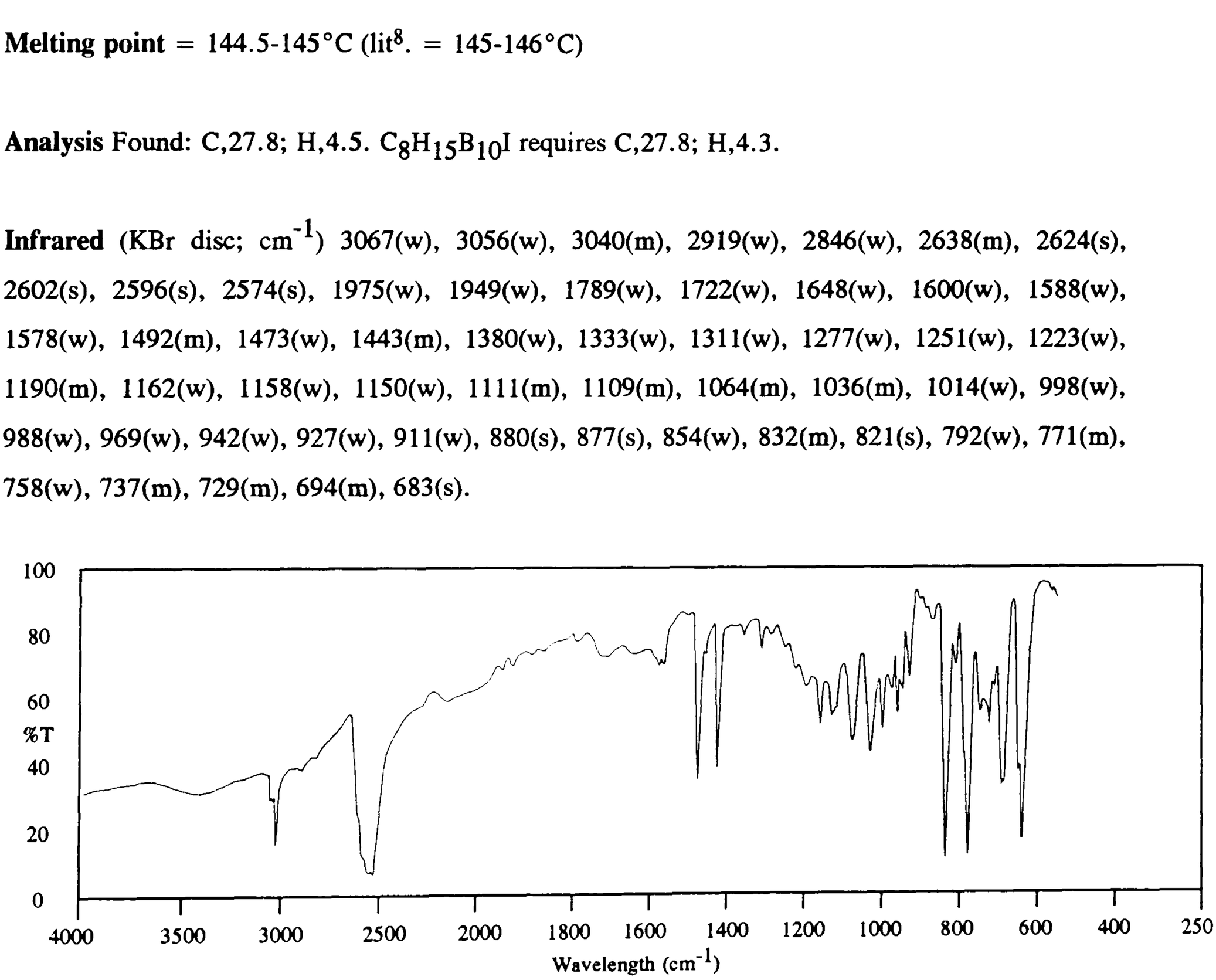
Mass spectrum (E.I.) A highest mass peak was observed at m/e 348 corresponding to the species $^{12}C_8{}^{1}H_{15}{}^{11}B_{10}{}^{127}I$, accompanied by the usual carborane isotope distribution pattern between m/e 342 and 348. A group of peaks were observed between m/e 215 and 221 from $C_8H_{15}B_{10}$.

12-iodo-1-phenyl-1,2-dicarba-*closo*-dodecaborane

Melting point = 144.5-145°C (lit[8]. = 145-146°C)

Analysis Found: C,27.8; H,4.5. $C_8H_{15}B_{10}I$ requires C,27.8; H,4.3.

Infrared (KBr disc; cm^{-1}) 3067(w), 3056(w), 3040(m), 2919(w), 2846(w), 2638(m), 2624(s), 2602(s), 2596(s), 2574(s), 1975(w), 1949(w), 1789(w), 1722(w), 1648(w), 1600(w), 1588(w), 1578(w), 1492(m), 1473(w), 1443(m), 1380(w), 1333(w), 1311(w), 1277(w), 1251(w), 1223(w), 1190(m), 1162(w), 1158(w), 1150(w), 1111(m), 1109(m), 1064(m), 1036(m), 1014(w), 998(w), 988(w), 969(w), 942(w), 927(w), 911(w), 880(s), 877(s), 854(w), 832(m), 821(s), 792(w), 771(m), 758(w), 737(m), 729(m), 694(m), 683(s).

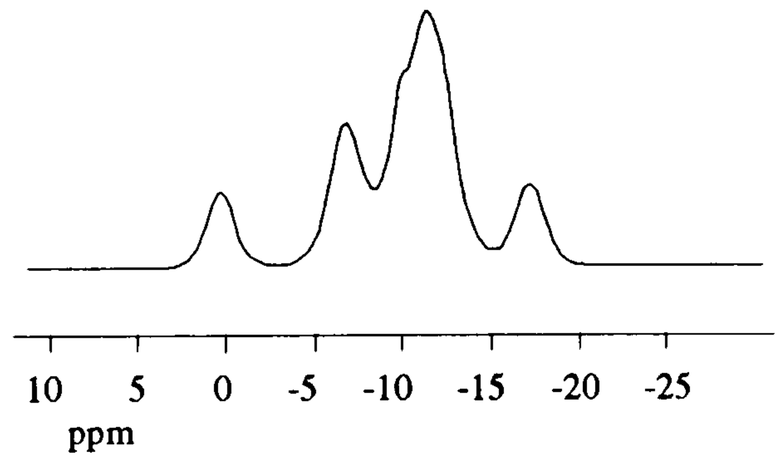


^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

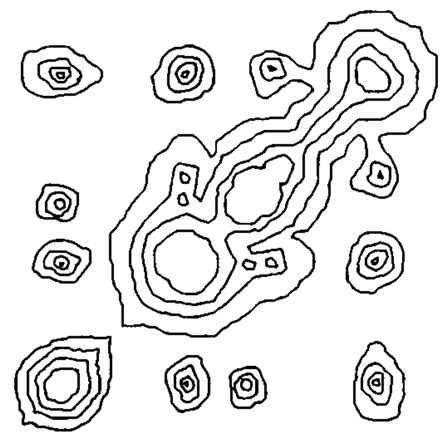
δ_{ppm}	intensity	type of peak	position of proton
7.45-7.31	5	multiplet	aromatic C(a,b,c)-H
4.06	1	broad singlet	carboranyl C(f)-H
4.0-1.3	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent C_6D_6, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-0.09	1	9
-6.71	2	8,10
-10.70	2	4,5
-11.17	4	3,6,7,11
-16.38	1	12

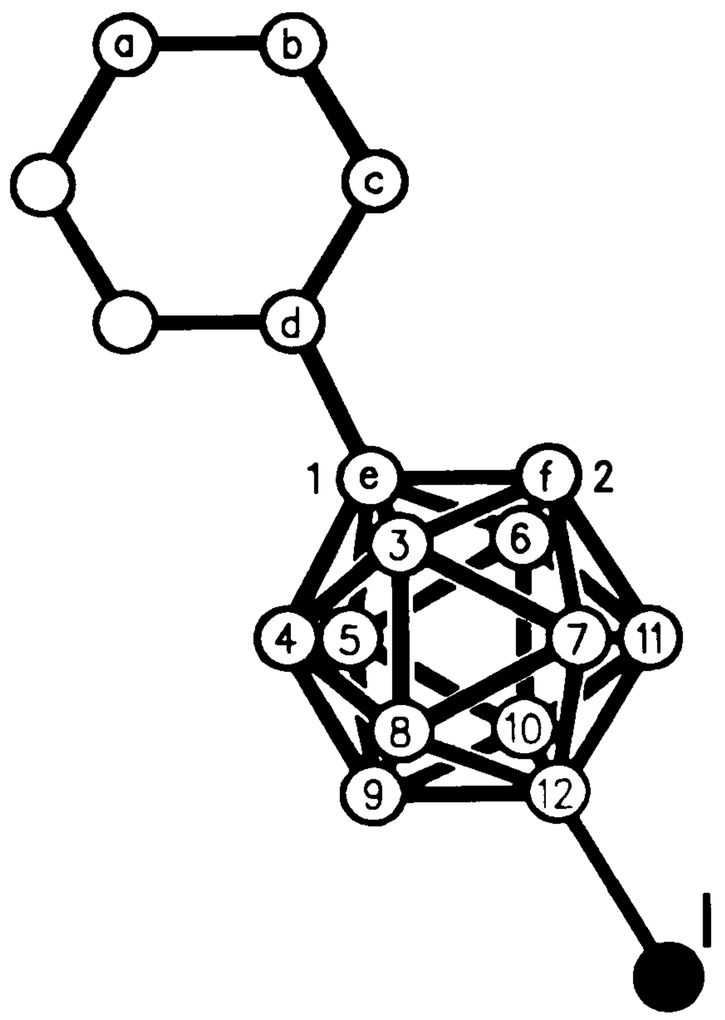


2D COSY



^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
132.68	d
130.27	b
129.01	a
127.41	c
73.28	e
61.00	f



9-iodo-1-phenyl-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

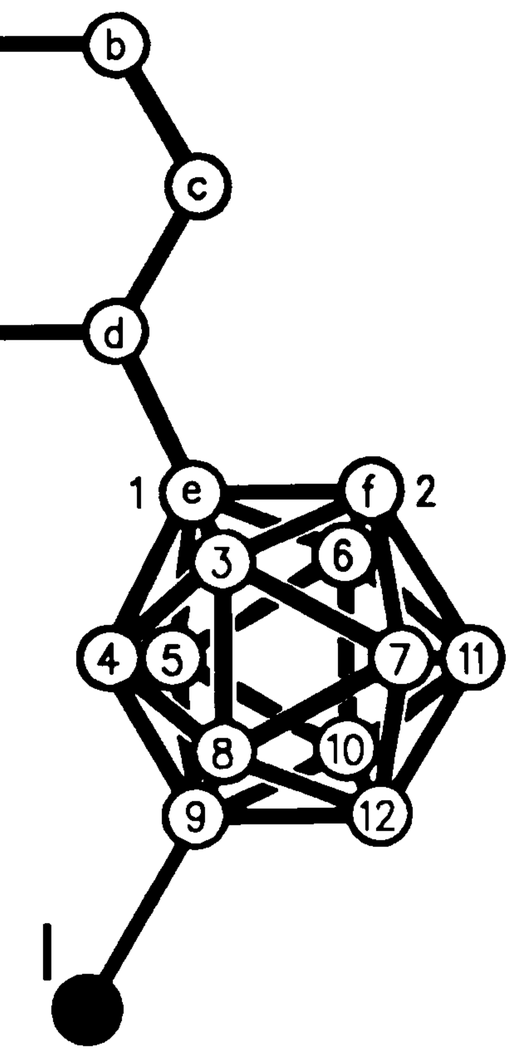
δ_{ppm}	intensity	type of peak	position of proton
7.51-7.32	5	multiplet	aromatic C(a,b,c)-H
4.29	1	broad singlet	carboranyl C(f)-H
4.0-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

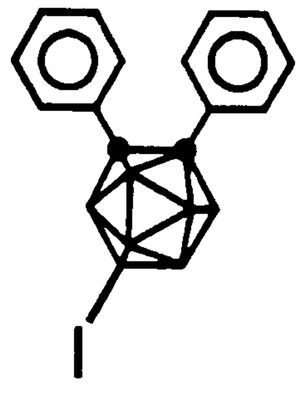
δ_{ppm}	intensity	position of boron
-4.47	1	12
-8.66	2	8,10
-11.88	4	3,6,4,5
-12.78	2	7,11
-17.55	1	9

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
132.23	d
130.32	b
129.01	a
127.40	c
77.38	e
56.58	f



9-iodo-1,2-diphenyl-1,2-dicarba-*closo*-dodecaborane

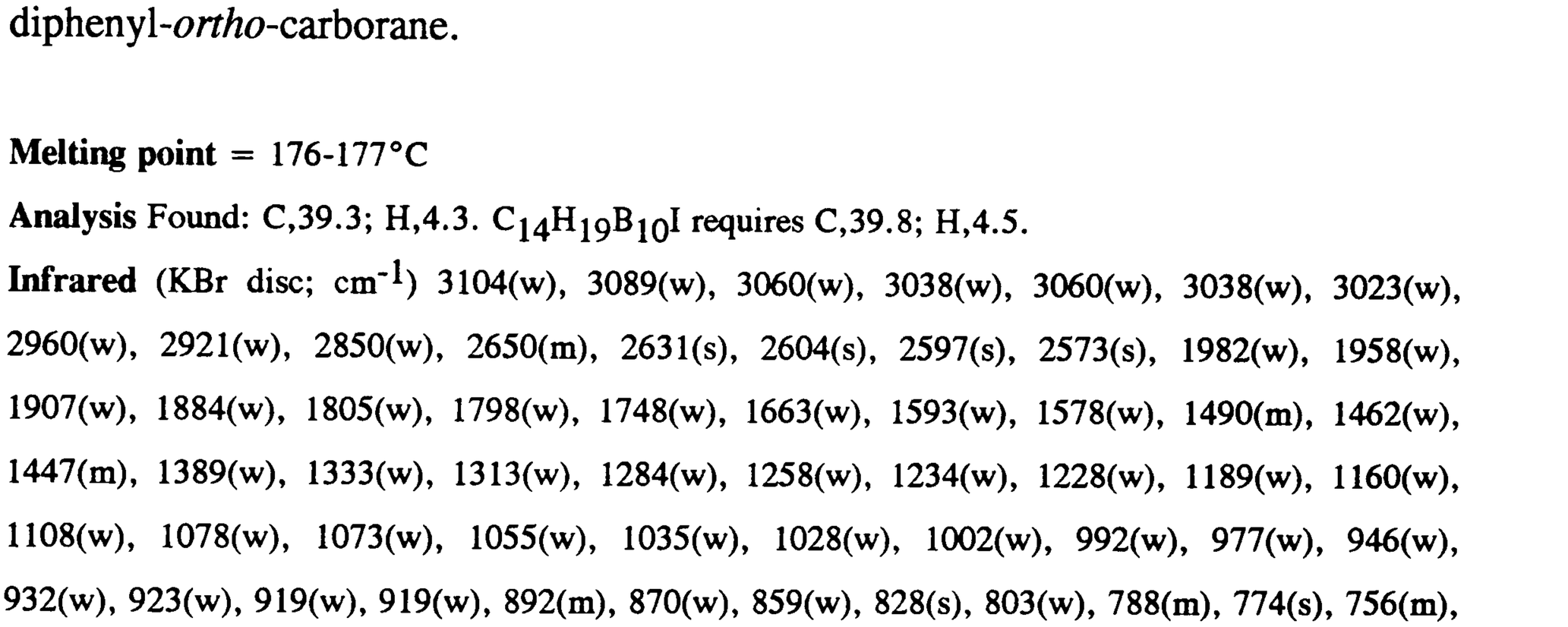


With method B, 2.96g (10 mmoles) 1,2-diphenyl-*ortho*-carborane, 1.27g (5 mmoles) sublimed iodine and 20ml of nitric acid / sulphuric acid mixture in 40ml glacial acetic acid at 40°C for 80 minutes gave 3.67g (87%) of 9-iodo-1,2-diphenyl-*ortho*-carborane.

Melting point = 176-177°C

Analysis Found: C,39.3; H,4.3. $C_{14}H_{19}B_{10}I$ requires C,39.8; H,4.5.

Infrared (KBr disc; cm^{-1}) 3104(w), 3089(w), 3060(w), 3038(w), 3060(w), 3038(w), 3023(w), 2960(w), 2921(w), 2850(w), 2650(m), 2631(s), 2604(s), 2597(s), 2573(s), 1982(w), 1958(w), 1907(w), 1884(w), 1805(w), 1798(w), 1748(w), 1663(w), 1593(w), 1578(w), 1490(m), 1462(w), 1447(m), 1389(w), 1333(w), 1313(w), 1284(w), 1258(w), 1234(w), 1228(w), 1189(w), 1160(w), 1108(w), 1078(w), 1073(w), 1055(w), 1035(w), 1028(w), 1002(w), 992(w), 977(w), 946(w), 932(w), 923(w), 919(w), 919(w), 892(m), 870(w), 859(w), 828(s), 803(w), 788(m), 774(s), 756(m), 741(w), 719(w), 700(w), 689(s), 662(w), 617(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 424 corresponding to the species $^{12}C_{14}{}^{1}H_{19}{}^{11}B_{10}{}^{127}I$, accompanied by the usual carborane isotope distribution pattern between m/e 418 and 424. Peaks present at m/e 291-297 were identified as $C_{14}H_{19}B_{10}$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

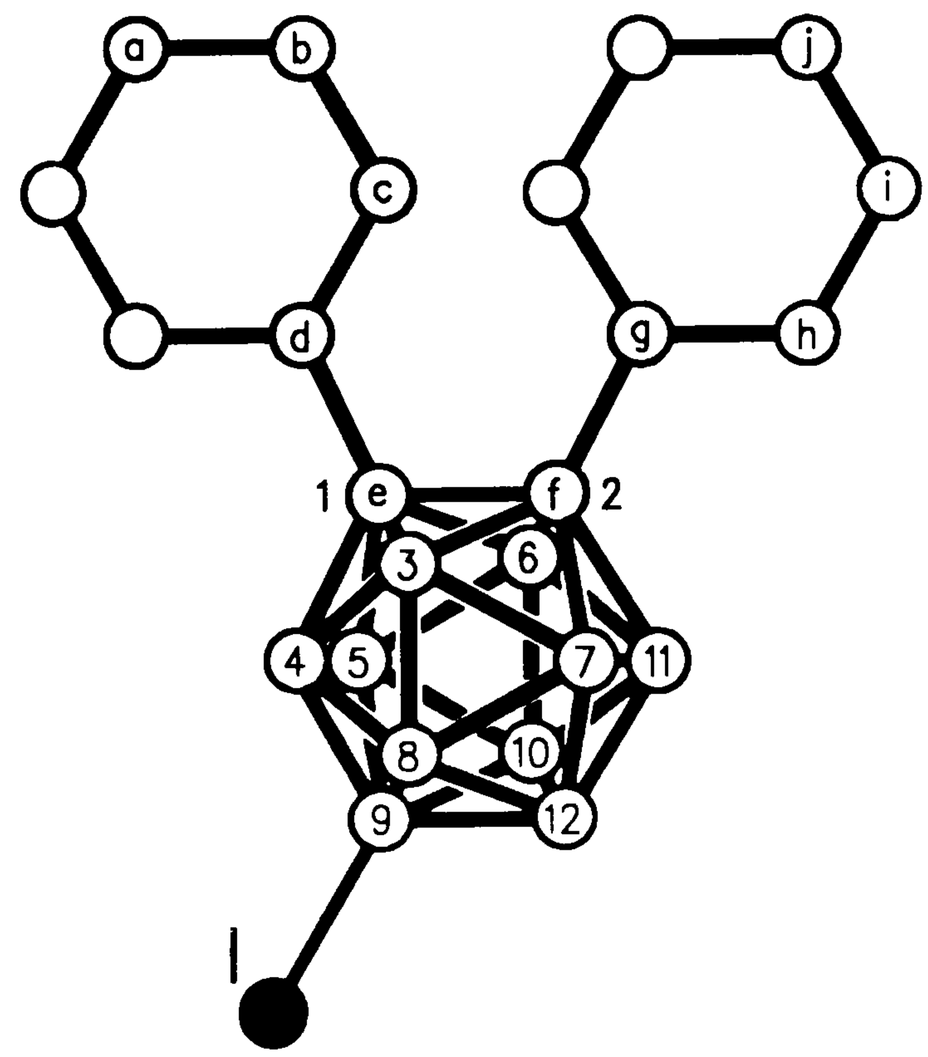
δ_{ppm}	intensity	type of peak	position of proton
7.42-7.11	10	multiplet	aromatic C(a,b,c)-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm. Peak assignments based on peak shapes.

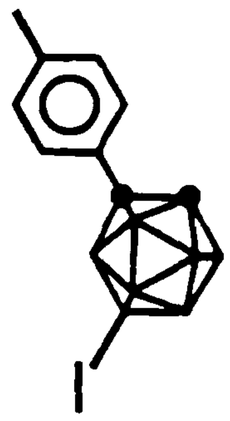
δ_{ppm}	intensity	position of boron
-2.35	1	12
-10.12	6	4,5,7,11,8,10
-12.32	2	3,6
-16.72	1	9

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

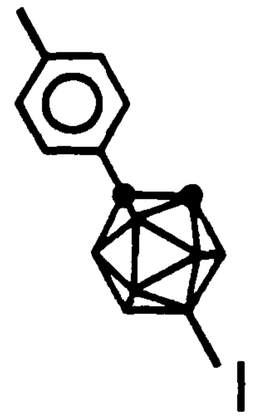
δ_{ppm}	position of carbon
130.46	a,c,d,g,h,j
128.41	b,i
85.85	f
81.94	e



Iodination of 1-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane



9- isomer

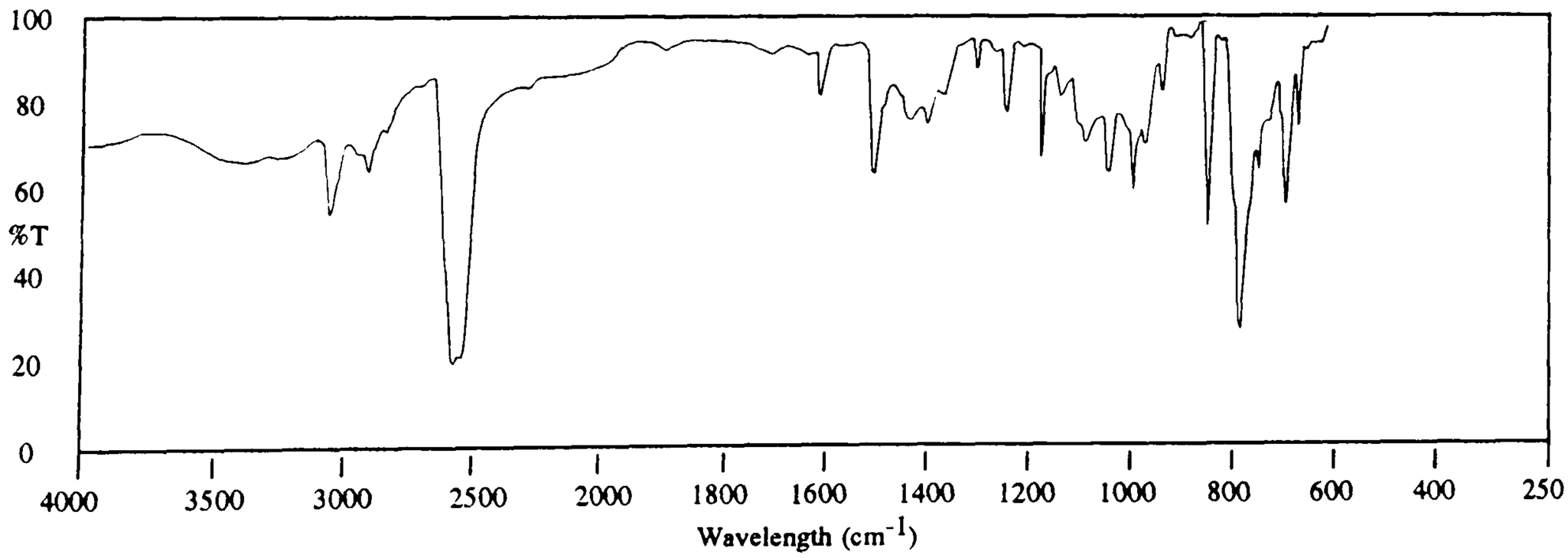


12- isomer

Using method B, 2.34g (10 mmoles) of 1-(4-methylphenyl)-*ortho*-carborane, 1.27g (5 mmoles) of sublimed iodine and 15ml of nitric acid / sulphuric acid mixture in 40ml of glacial acetic acid at 80°C for 45 minutes gave 3.17g (88%) of a mixture of iodo-1-(4-methylphenyl)-*ortho*-carborane isomers. Gas chromatography showed three peaks at 31.5(10%), 32.1(46%) and 32.4 minutes (44%) probably from 8-, 9- and 12 isomers respectively. These isomers could not be separated by preparative gas, thin layer or column chromatography. The ^{1}H, ^{11}B and ^{13}C N.M.R. peaks of 9- and 12- isomers, however, can be assigned with the help of boron-iodo 1-phenyl-*ortho*-carborane data.

Analysis Found: C,30.1; H,4.6. $C_9H_{17}B_{10}I$ requires C,30.0; H,4.7.

Infrared (KBr disc; cm^{-1}) 3058(m), 3038(w), 2952(w), 2917(w), 2853(w), 2593(s), 2575(s), 1612(w), 1511(m), 1509(m), 1462(w), 1445(w), 1432(w), 1412(w), 1380(w), 1319(w), 1282(w), 1262(w), 1196(m), 1181(w), 1160(w), 1131(w), 1113(m), 1070(m), 1049(w), 1022(m), 1000(m), 992(w), 968(w), 946(w), 913(w), 903(w), 880(m), 856(w), 830(m), 819(s), 800(m), 783(m), 763(w), 731(m), 708(w), 693(w), 662(w), 618(w), 566(w), 548(w), 500(m).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 362 corresponding to the species $^{12}C_9{}^{1}H_{17}{}^{11}B_{10}{}^{127}I$, accompanied by the usual carborane isotope distribution pattern between m/e 356 and 362. Fragment from peaks observed between m/e 229 and 235 was $C_9H_{17}B_{10}$.

12-iodo-1-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

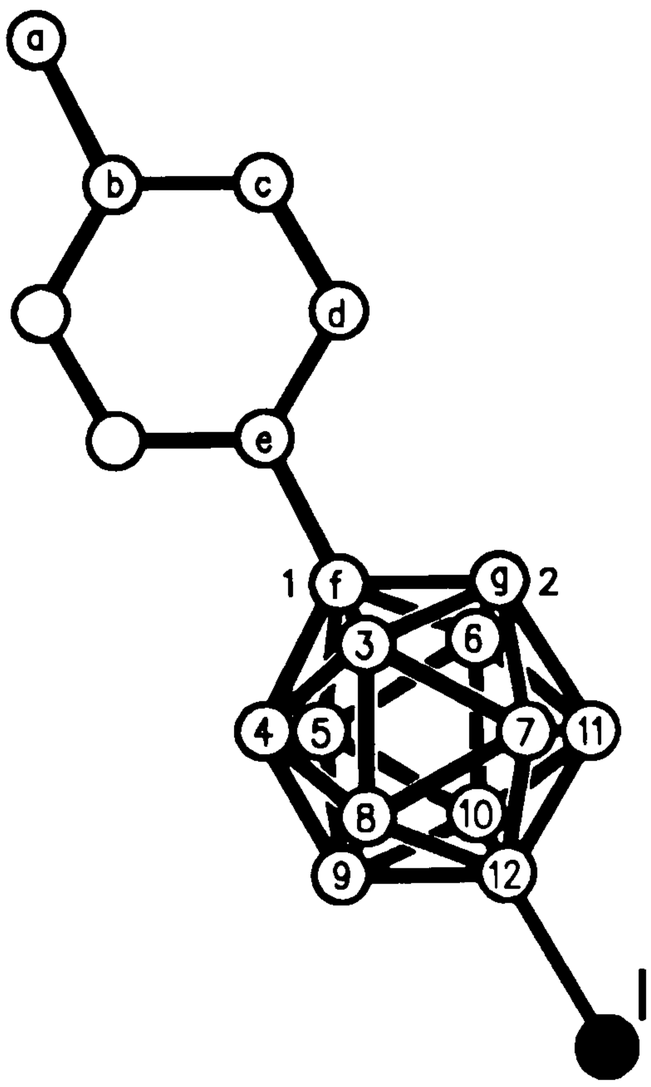
δ_{ppm}	intensity	type of peak	position of proton
7.35 7.32 7.16 7.13	4	doublet of doublets	aromatic C(c,d)-H
4.00	1	broad singlet	carboranyl C(g)-H
2.35	3	singlet	methyl C(a)-H
4.0-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-1.84	1	9
-8.81	2	8,10
-12.81	2	4,5
-13.87	4	3,6,7,11
-18.53	1	12

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
140.66	b
129.64	d
129.44	e
127.41	c
73.51	f
61.27	g
20.96	a



9-iodo-1-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

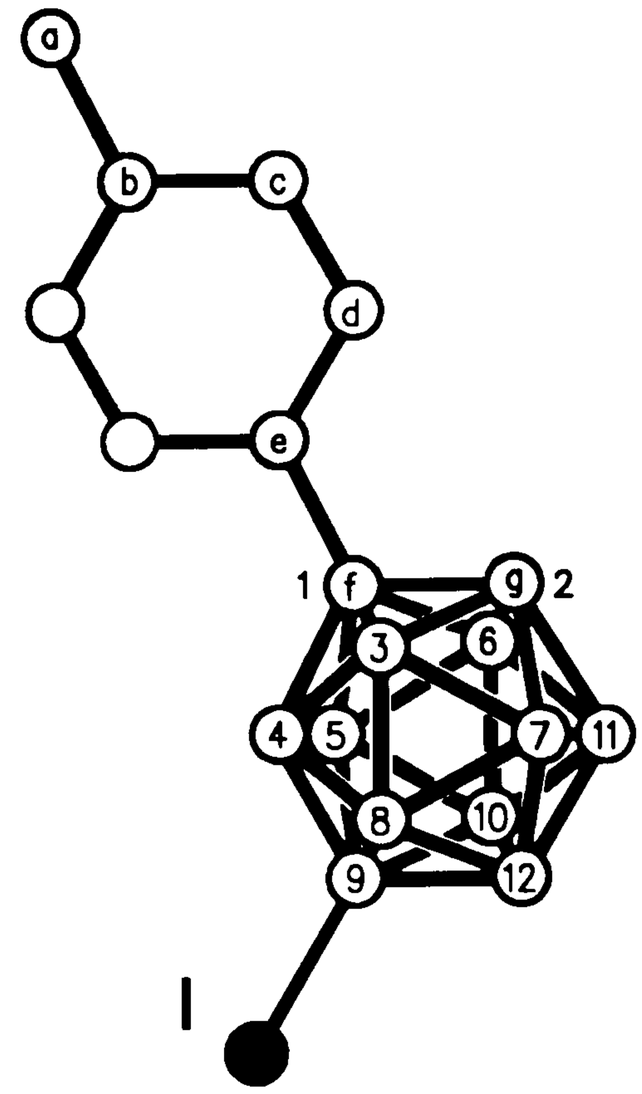
δ_{ppm}	intensity	type of peak	position of proton
7.39 7.36 7.18 7.15	4	doublet of doublets	aromatic C(c,d)-H
4.22	1	broad singlet	carboranyl C(g)-H
2.35	3	singlet	methyl C(a)-H
4.0-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-4.73	1	12
-8.81	2	8,10
-12.81	4	3,6,4,5
-13.87	2	7,11
-17.62	1	9

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
140.66	b
129.64	d,e
127.41	c
77.18	f
56.76	g
20.96	a



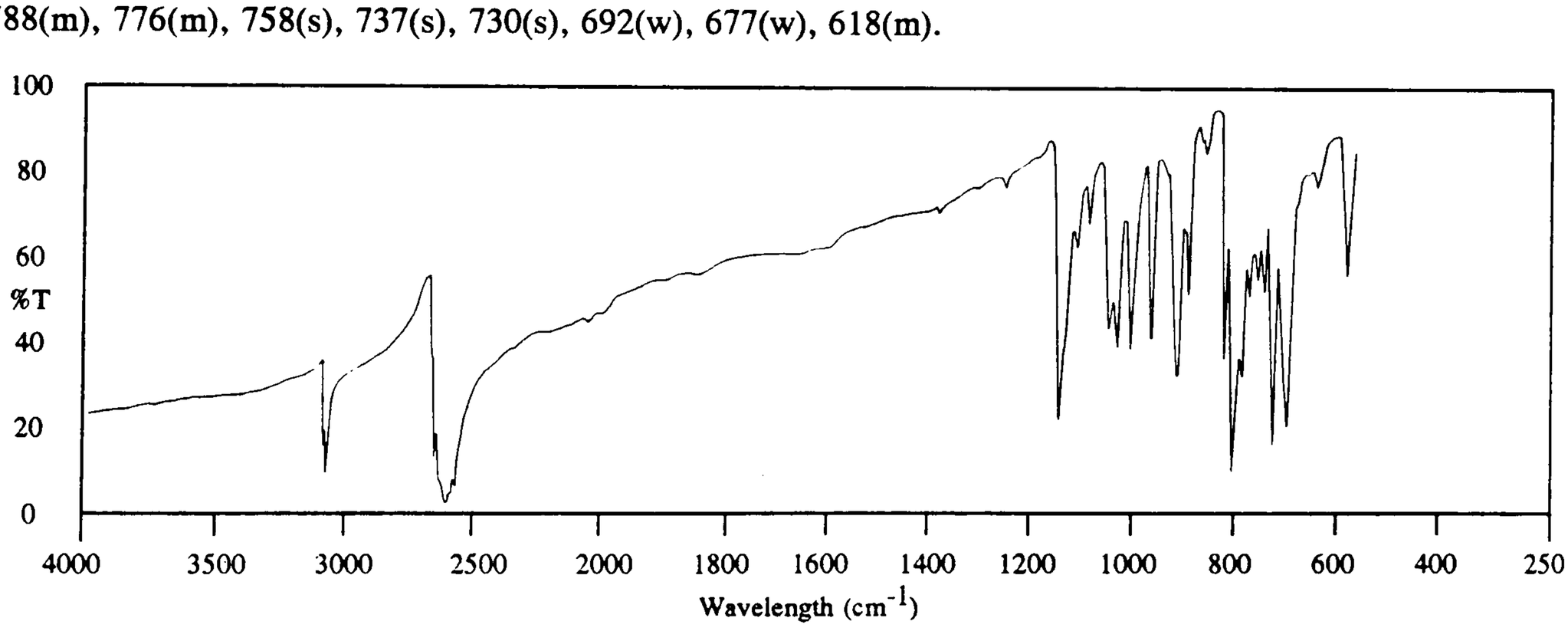
9-iodo-1,7-dicarba-*closo*-dodecaborane

Using method B, 1.44g (10 mmoles) *meta*-carborane, 1.27g (5 mmoles) sublimed iodine and 20ml of nitric acid / sulphuric acid mixture in 40ml glacial acetic acid at 80°C for 45 minutes gave 2.26g (84%) of 9-iodo-*meta*-carborane.

Melting point = 109-110°C (lit[16]. = 110-111°C)

Analysis Found: C,9.0; H,4.3. $C_2H_{11}B_{10}I$ requires C,8.9; H,4.1.

Infrared (KBr disc; cm^{-1}) 3060(s), 3050(s), 2652(s), 2636(s), 2613(s), 2595(s), 2578(s), 2095(w), 1388(w), 1264(w), 1163(s), 1158(s), 1131(w), 1109(w), 1070(m), 1054(m), 1028(m), 990(m), 962(w), 944(m), 940(m), 925(w), 918(m), 894(w), 887(w), 850(m), 835(s), 817(m), 802(m), 788(m), 776(m), 758(s), 737(s), 730(s), 692(w), 677(w), 618(m).



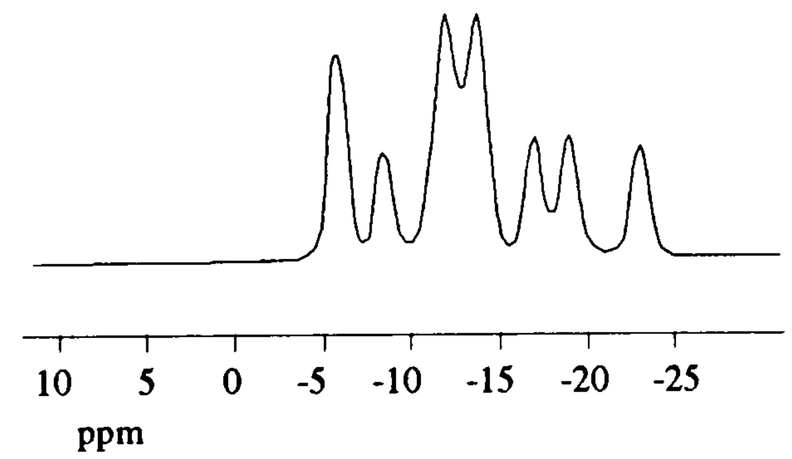
Mass spectrum (E.I.) A highest mass peak was observed at m/e 272 corresponding to the species $^{12}C_2{}^{1}H_{11}{}^{11}B_{10}{}^{127}I$, accompanied by the usual carborane isotope distribution pattern between m/e 266 and 272. A group of peaks was also seen between m/e 139 and 145 identified as $C_2H_{11}B_{10}$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

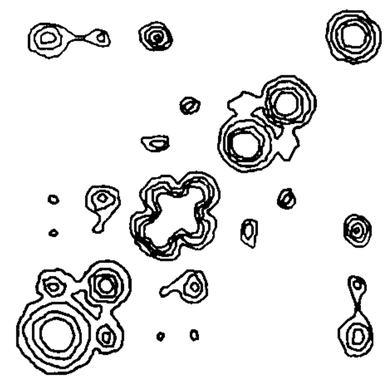
δ_{ppm}	intensity	type of peak	position of proton
2.97	2	broad singlet	carboranyl C-H
4.1-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-5.81	2	5,12
-8.64	1	10
-12.26	2	4,8
-13.36	2	6,11
-17.15	1	3
-19.16	1	2
-23.83	1	9

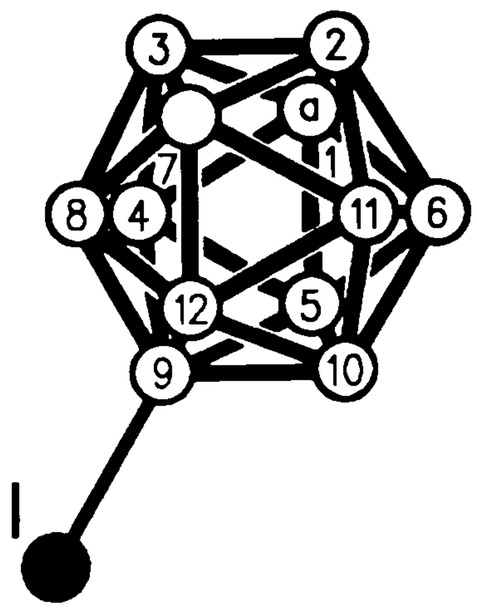


2D COSY

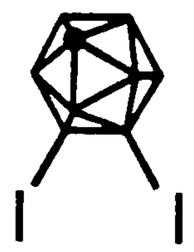


^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
56.22	a



9,10-diiodo-1,7-dicarba-*closo*-dodecaborane

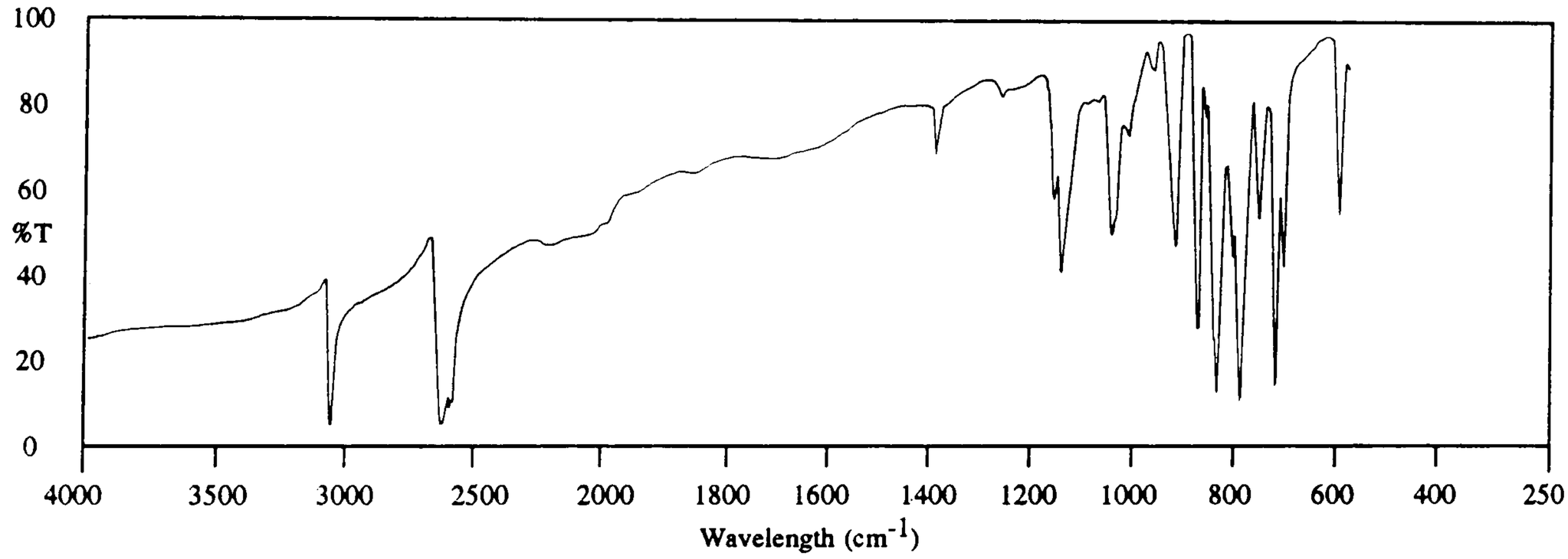


With method B, 1.44g (0.01 moles) *meta*-carborane, 2.54g (0.01 moles) sublimed iodine and 30ml of nitric acid / sulphuric acid mixture in 40ml of glacial acetic acid at 80°C for three hours produced 3.25g (82%) of 9,10-diiodo-*meta*-carborane.

Melting point = 187-188°C (lit[16]. = 189-190°C)

Analysis Found: C,6.5; H,2.7. $C_2H_{10}B_{10}I_2$ requires C,6.1; H,2.5.

Infrared (KBr disc; cm^{-1}) 3041(s), 2625(s), 2597(s), 2589(s),1387(w), 1264(w), 1167(w), 1151(m), 1146(m), 1108(w), 1083(w), 1060(m), 1057(m), 1030(w), 1025(w), 986(w), 980(w), 942(m), 939(s), 920(w), 898(s), 881(w), 868(s), 861(s), 832(m), 817(s), 778(m), 749(s), 732(m), 700(w), 692(w), 674(w), 622(m).



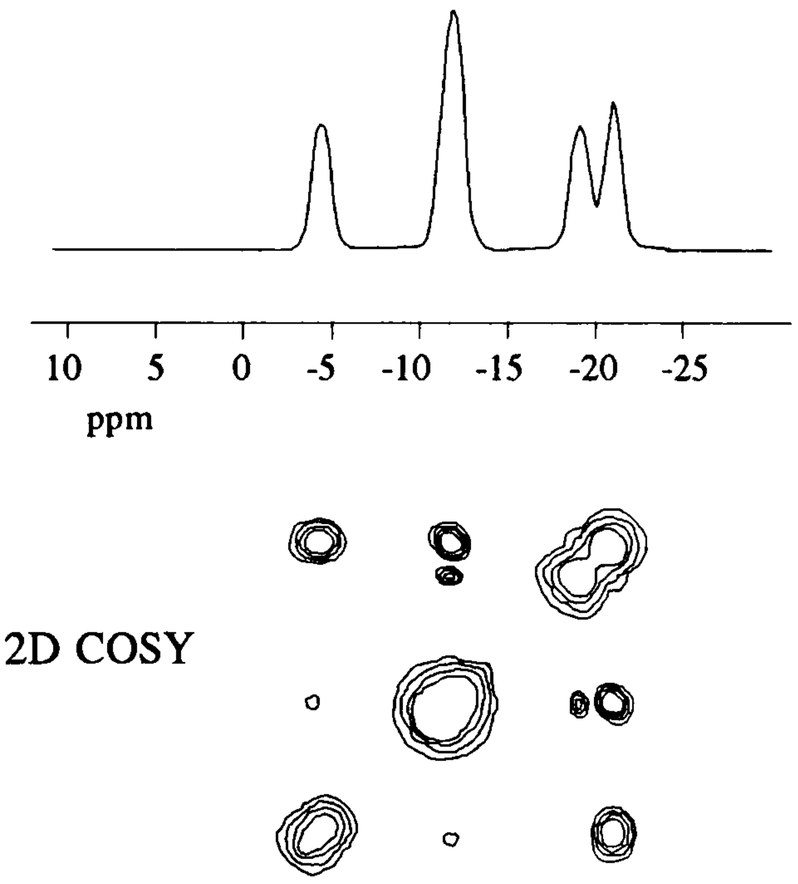
Mass spectrum (E.I.) A highest mass peak was observed at m/e 398 corresponding to the species $^{12}C_2{}^{1}H_{10}{}^{11}B_{10}{}^{127}I_2$, accompanied by the usual carborane isotope distribution pattern between m/e 392 and 398. A group of peaks between m/e 265 and 271 was observed and the fragment identified as $C_2H_{10}B_{10}I$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
3.15	2	broad singlet	carboranyl C-H
4.2-1.0	8	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

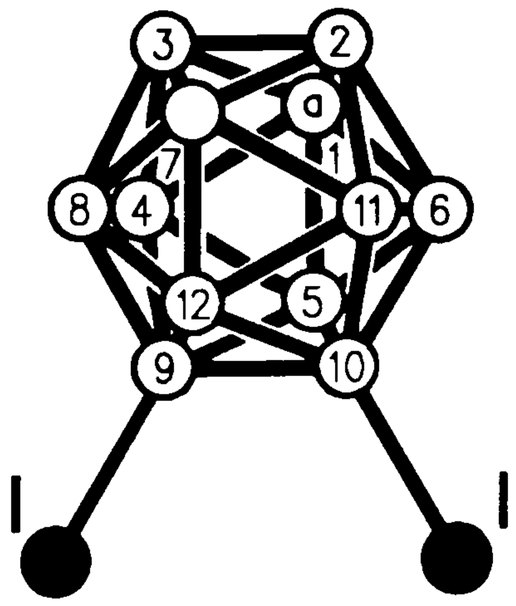
δ_{ppm}	intensity	position of boron
-4.41	2	5,12
-12.16	4	4,6,8,11
-19.01	2	2,3
-20.81	2	9,10



2D COSY

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
56.73	a



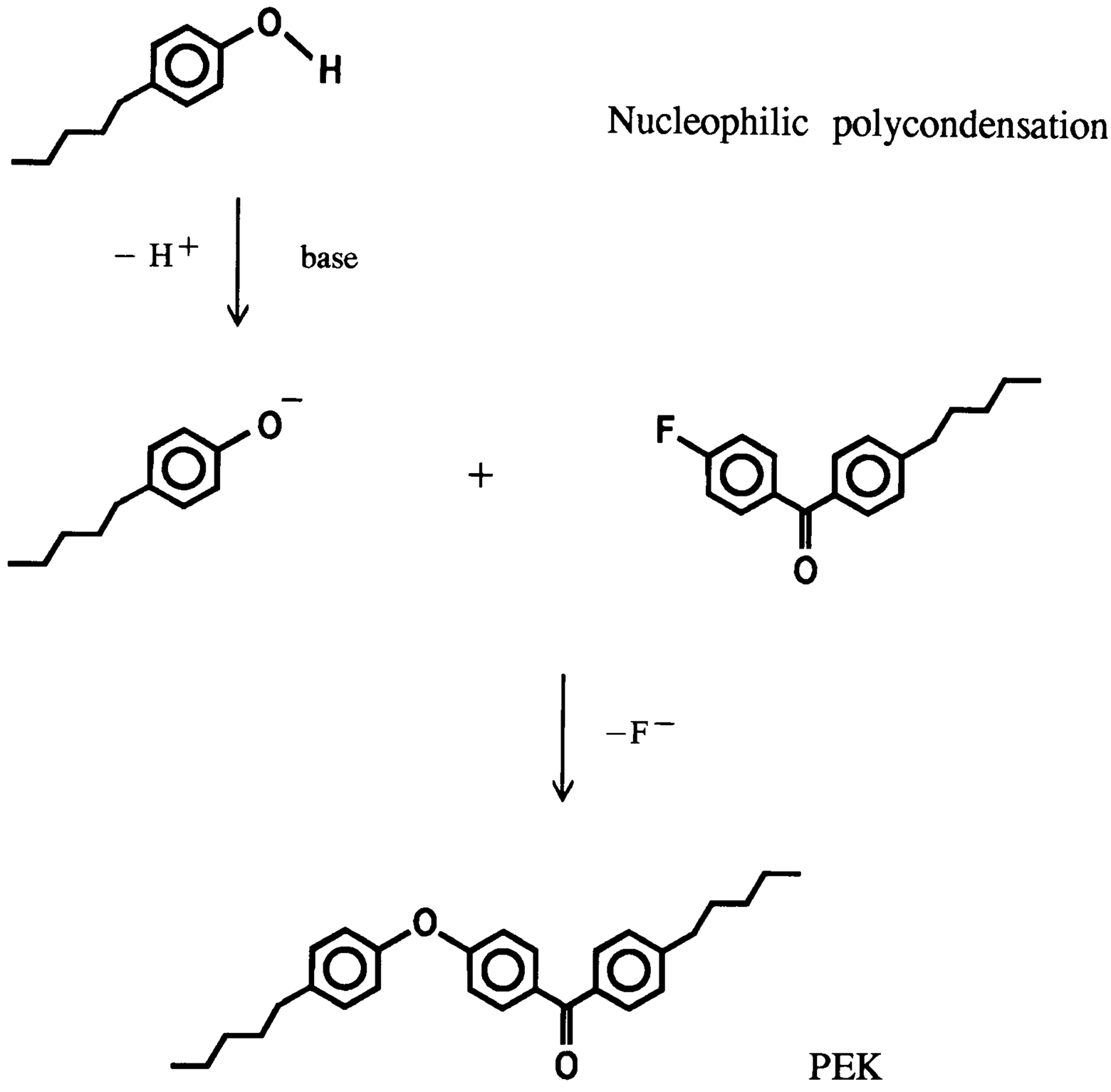
CHAPTER 6

BORON-ARYL CARBORANES

This chapter contains a literature review of polyaryletherketones (PEKs), monomer suitability for carborane-containing polyaryletherketones (CPEKs), formation and reactions of boron-aryl carboranes. It also describes monomer syntheses and model reactions of boron-aryl carboranes carried out in this study.

POLYARYLETHERKETONES (PEKs)

Polyaryletherketones are usually produced by nucleophilic or electrophilic polycondensation. Nucleophilic polycondensation is carried out using base as reagent on suitable bisphenols and aromatic difluorides to form ether links[1,2].



Electrophilic polycondensation occurs using an acid as reagent on suitable aromatic dicarboxylic acids and aromatic ethers[3,4]. Low molecular weight PEKs are formed using common organic solvents as PEKs are insoluble in these

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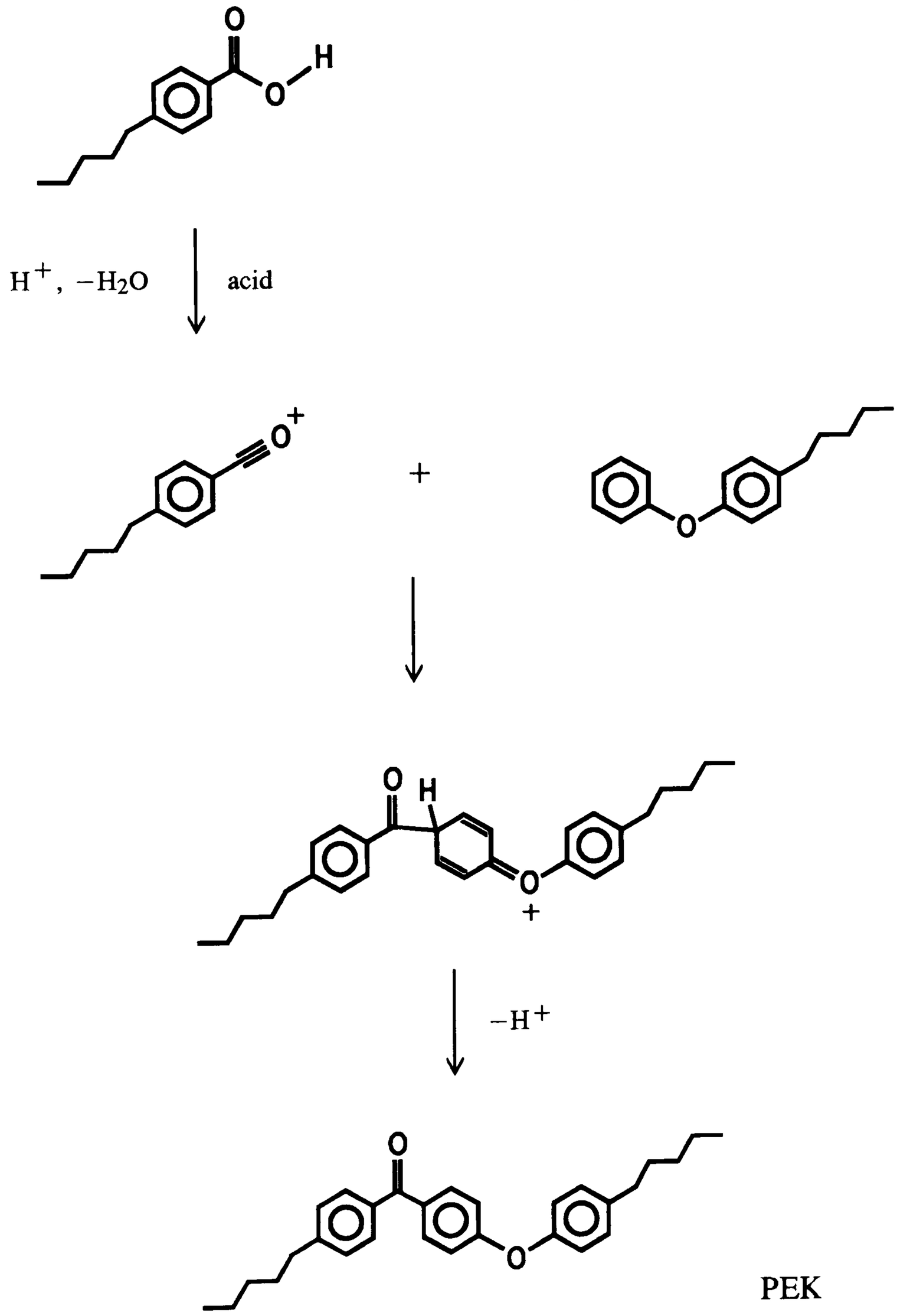
1. Johnson R.N. Farnham A.G. Clendinning R.A. Hale W.F. Merriam C.N. *J. Polym. Sci. A1* 1967 **5** 2375-2398
2. Attwood T.E. Dawson P.C. Freeman J.L. Hoy L.R.J. Rose J.B. Staniland P.A. *Polymer* 1981 **22** 1096-1103
3. Colquhoun H.M. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* 1984 **25** 17-18
4. Colquhoun H.M. Lewis D.F. *Polymer* 1988 **29** 1902-1908

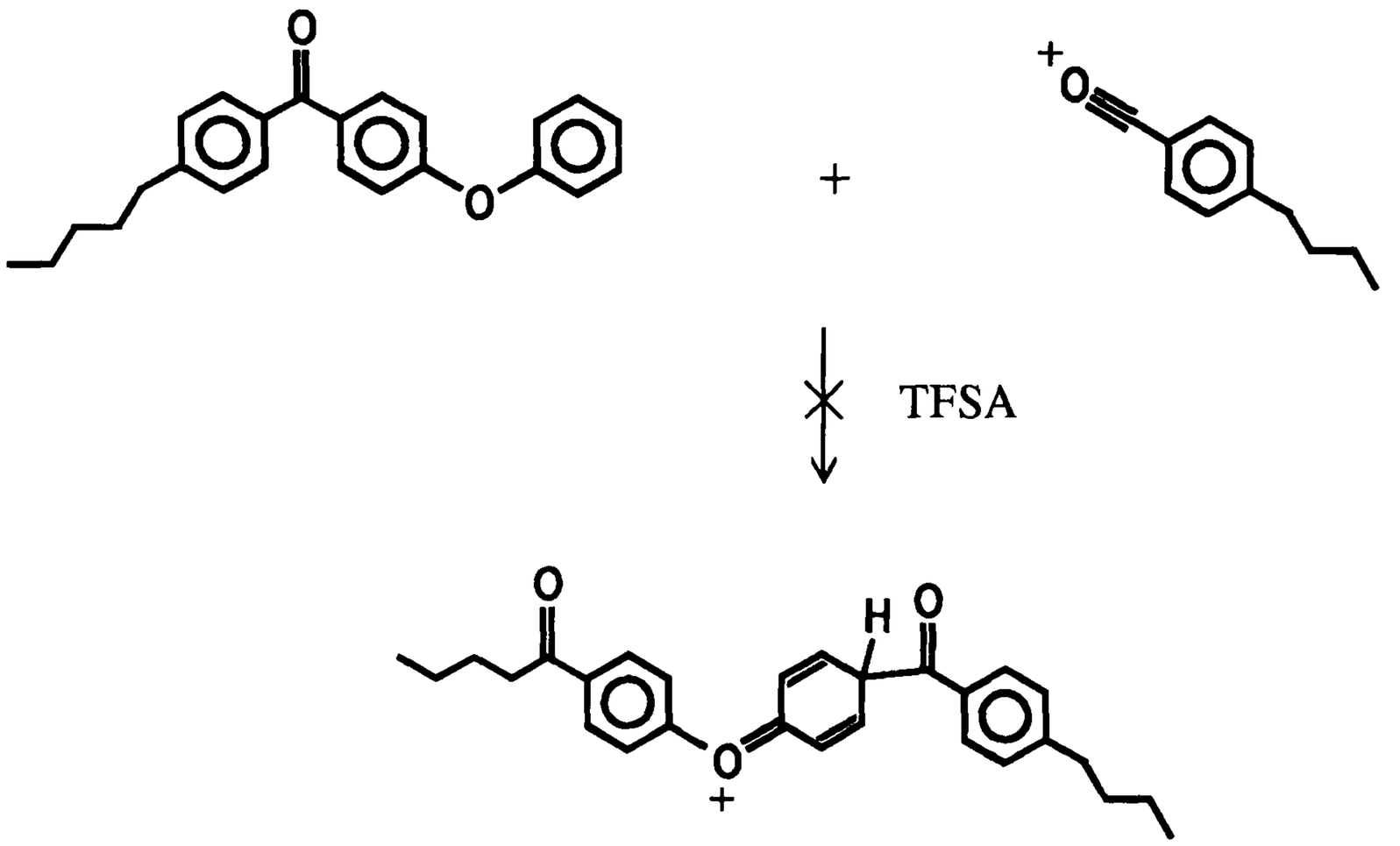
solvents[2]. Diphenyl sulphone, $(C_6H_5)_2SO_2$, and trifluoromethanesulphonic acid (TFSA), CF_3SO_3H, are best used for nucleophilic and electrophilic PEK polycondensation respectively as high molecular weight PEKs are soluble in these solvents[3,4]. TFSA is also a superacid so it can also act as reagent for electrophilic PEK polycondensation.

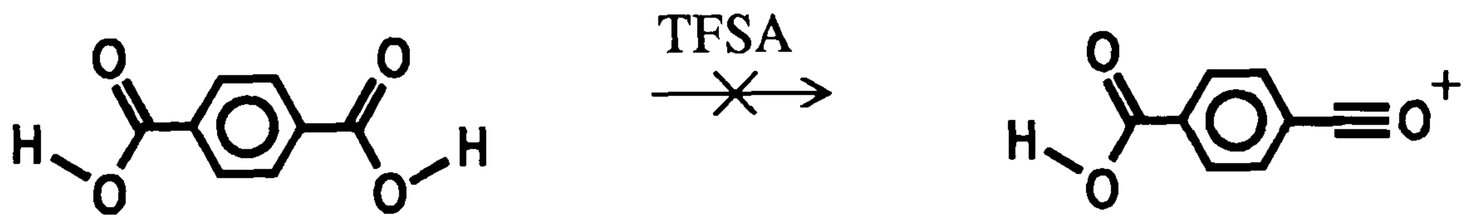
Electrophilic polycondensation



PEK

There are restrictions on monomer suitability for PEK formation using TFSA. Diphenyl ether is not suitable as a monomer for PEK formation due to the deactivating effect of the carbonyl group on the second reaction site of the ether molecule. Terephthalic acid is also an unfavourable monomer, it fails to form a cation because of the electron-withdrawing effect of the carboxylic acid group.





PEKs can also be formed by electrophilic polydehydrochlorination using an aromatic ether such as diphenyl ether and aromatic acyl dichloride like terephthaloyl chloride as monomers in polyphosphoric acid[5]. This route, however, gives lower molecular weight PEKs than PEKs obtained from polycondensations above.

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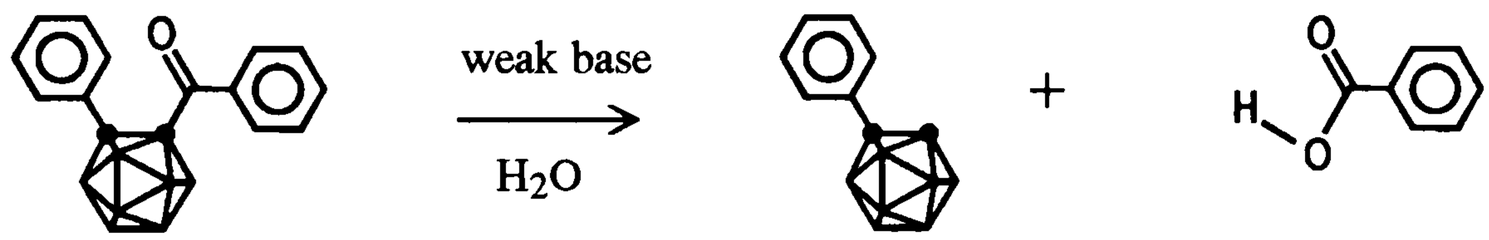
5. Iwakura Y. Uno K. Takiguchi T. *J. Polym. Sci. A1* 1968 6 3345-3355

CARBORANE-CONTAINING POLYARYLETHERKETONES (CPEKs)

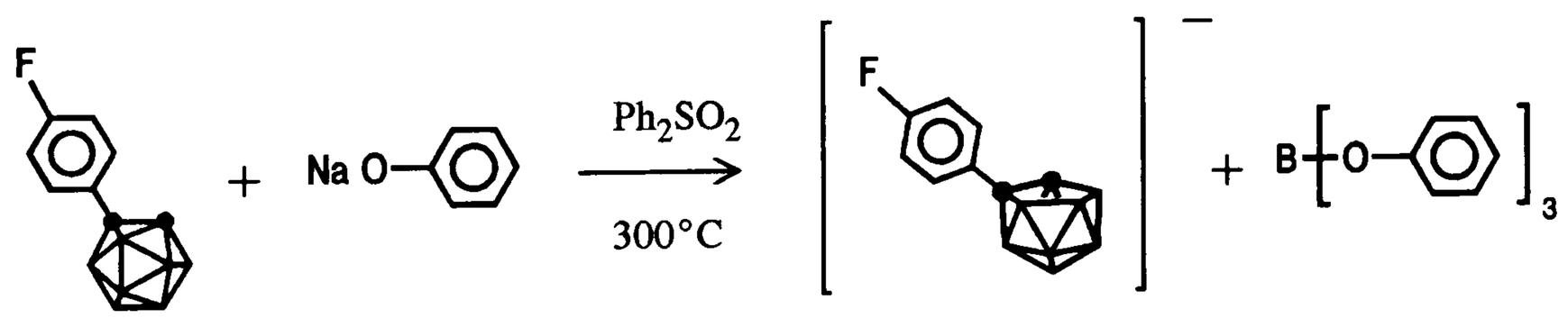
Suitable monomers for carborane-containing polyaryletherketones (CPEKs) need to be stable to hydrolysis. Carboranes with an ether group bonded to the cage carbon are not known and with a ketone group are susceptible to hydrolysis[6]. A phenylene group between the cage and functional group gives carboranes which are hydrolytically stable.



1-C_6H_5-2-C_6H_5CO-1,2-$C_2B_{10}H_{10}$ → 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ + benzoic acid

Facile carboranyl-ketone bond cleavage by hydrolysis.

Model reactions were used to assess monomer suitability. A reaction between 1-(4-fluorophenyl)-*ortho*-carborane (**I**) and sodium phenoxide did not give the expected product 1-(4-phenoxyphenyl)-*ortho*-carborane, base degradation occurred instead[7a]. Nucleophilic polycondensation is therefore unsuitable for CPEK formation.



(**I**) → 7-(4-FC_6H_4)-7,8-$C_2B_9H_{11}^-$ + $B(OC_6H_5)_3$

By contrast, electrophilic condensation of 1-(4-phenoxyphenyl)-*ortho*-carborane (**II**) with benzoic acid in TFSA and 1-phenyl-2-(4-carboxyphenyl)-

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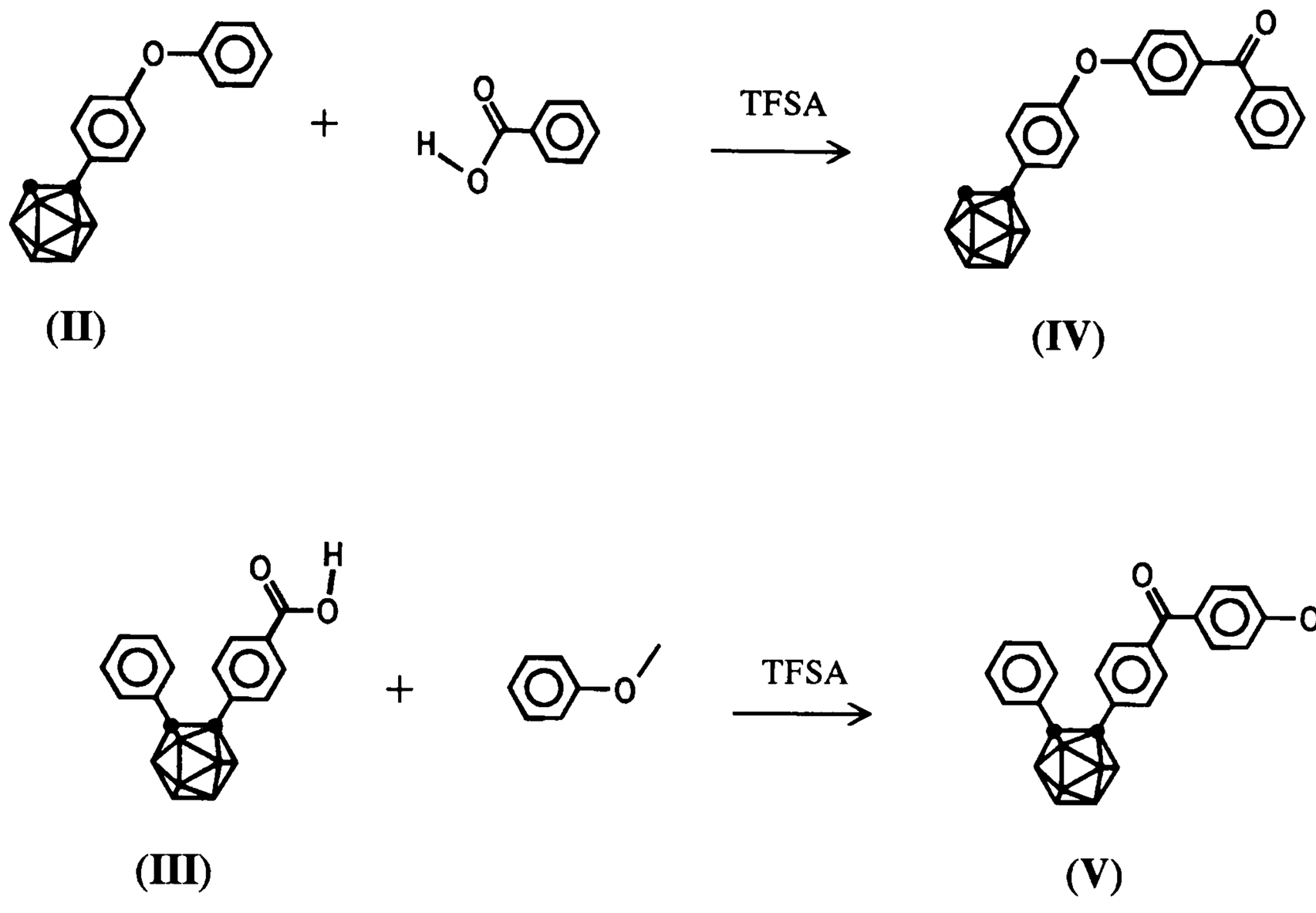
6. Stanko V.I. Klimova A.I. Chapovskii Yu.A. Klimova T.P. J. Gen. Chem. U.S.S.R. 1966 36 1773-1778
7. Stephenson I.R. "New Derivative and Polymer Chemistry of Icosahedral Carboranes" Ph.D. Thesis University of Durham Durham 1988 a) p60-63 b) p113-114 c) p93-94

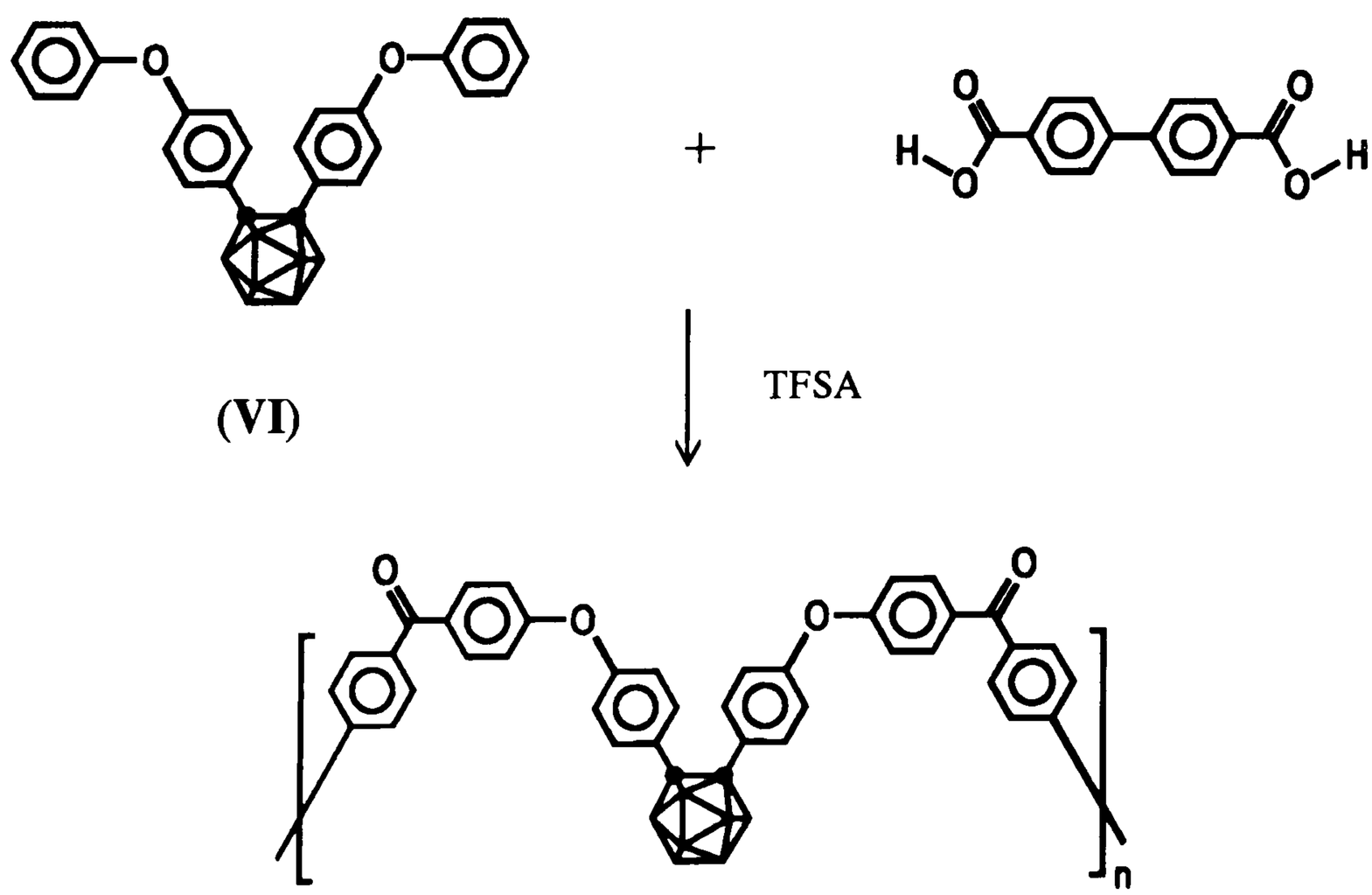
ortho-carborane (**III**) with anisole in TFSA gave the expected products, (**IV**) and (**V**), showing that electrophilic polycondensation is a viable route to CPEK.



(II) **(IV)**

(III) **(V)**

Four different CPEKs have been formed by electrophilic polycondensation with 1,2-bis(4-phenoxyphenyl)-*ortho*-carborane (**VI**) and 1,2-bis(4-carboxyphenyl)-*ortho*-carborane as carborane-containing monomers[7b].

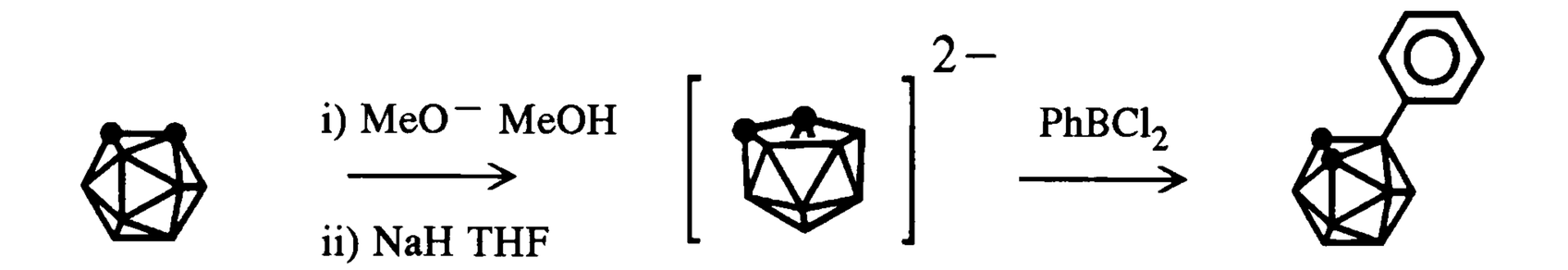


(VI)

Example of CPEK formation

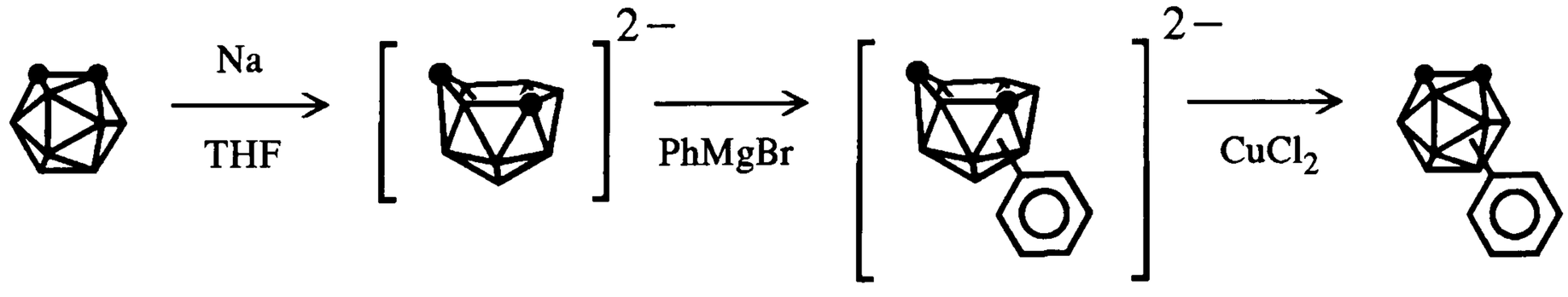
BORON-ARYL CARBORANES

Boron-aryl carboranes can be formed from parent carboranes via *nido* $C_2B_9H_{11}^{2-}$ anions with aryl boron dichlorides[8,9,10,11,12,13,14]. 3-aryl-*ortho*-carborane and 2-aryl-*meta*-carborane are obtained from *ortho*- and *meta*-carborane respectively.



$1,2\text{-}C_2B_{10}H_{12}$ $7,8\text{-}C_2B_9H_{11}^{2-}$ $3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{11}$

Dianions of *ortho*-carborane interact with aryl magnesium halides or aryl lithiums forming a mixture of boron-aryl-*ortho*-carborane isomers after oxidation with copper chloride[15]. *Para*-carborane dianions with the same reagents give boron-aryl-*meta*-carborane isomers[16].



$1,2\text{-}C_2B_{10}H_{12}$ $C_2B_{10}H_{12}^{2-}$ $C_6H_5\text{-}C_2B_{10}H_{11}^{2-}$ 3-, 4-, 8- or 9-C_6H_5-1,2-$C_2B_{10}H_{11}$

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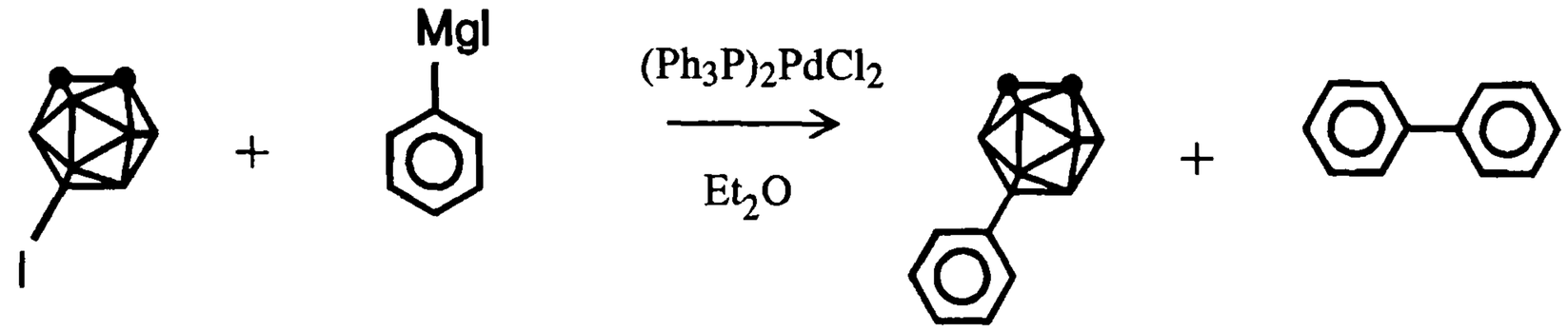
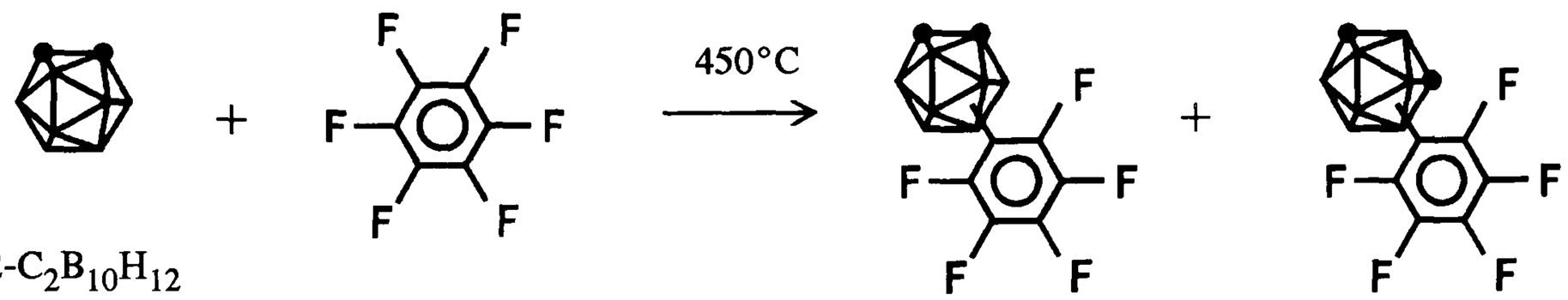
8. Hawthorne M.F. Wegner P.A. *J. Am. Chem. Soc.* 1965 **87** 4392-4393
9. Zakharkin L.I. Kukulina E.I. Podvisotskaya L.S. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1966 1808
10. Zakharkin L.I. Kalinin V.N. Shepilov I.P. *Dokl. Akad. Nauk. S.S.S.R.* 1967 **174** 606-609 (Russ) [CA68:39684e]
11. Hawthorne M.F. Wegner P.A. *J. Am. Chem. Soc.* 1968 **90** 896-901
12. Zakharkin L.I. Kalinin V.N. Snyakin A.P. Kvasov B.A. *J. Organometal. Chem.* 1969 **18** 19-26
13. Adler R.G. Hawthorne M.F. *J. Am. Chem. Soc.* 1970 **92** 6174-6182
14. Zakharkin L.I. Kalinin V.N. *J. Gen. Chem. U.S.S.R.* 1973 **43** 853-856
15. Kalinin V.N. Kobel'kova N.I. Astakhin A.V. Gusev A.I. Zakharkin L.I. *J. Organometal. Chem.* 1978 **149** 9-21
16. Kalinin V.N. Kobel'kova N.I. Astakhin A.V. Zakharkin L.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1977 2209-2211

9-aryl-*ortho*- and *meta*-carborane are best obtained from 9-iodo-*ortho*- and *meta*-carborane respectively[17,18,19]. The iodine atom is replaced with an aryl group from aryl magnesium iodide in the presence of a palladium catalyst. The reaction mechanism, shown overleaf, is found to be similar to palladium or nickel catalysed formation of diaryls[18,20].



9-I-1,2-$C_2B_{10}H_{11}$ 9-C_6H_5-1,2-$C_2B_{10}H_{11}$

Hexafluorobenzene reacts with *ortho*-carborane at 450°C to yield a mixture of boron-pentafluorophenyl-*ortho*- and *meta*-carborane isomers[21]. This is the only known direct formation of a boron-aryl carborane from a parent carborane.



1,2-$C_2B_{10}H_{12}$

3-. 4-, 8- or 9-

C_6F_5-1,2-$C_2B_{10}H_{11}$

2-. 4-, 5- or 9-

C_6F_5-1,7-$C_2B_{10}H_{11}$

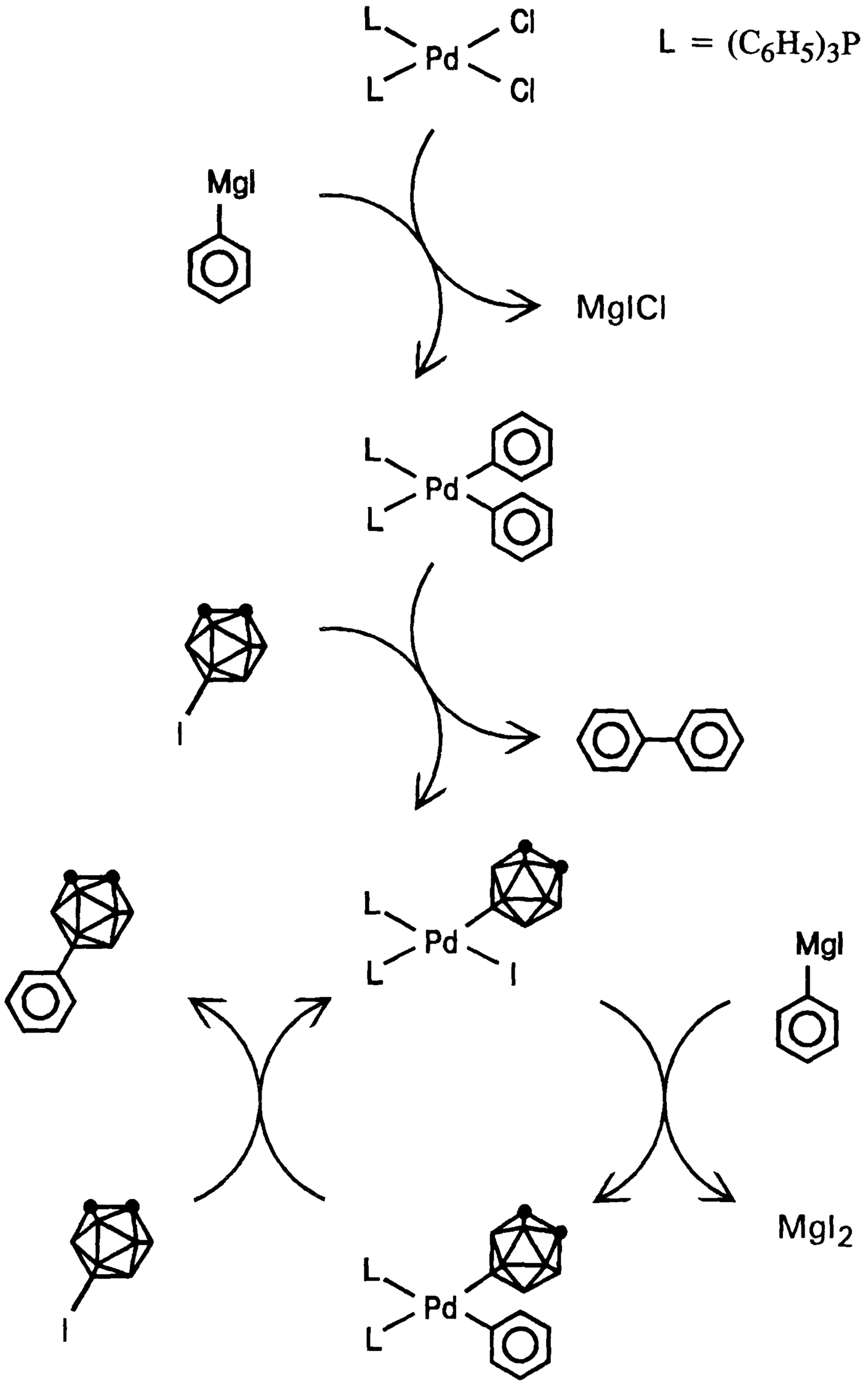
17. Zakharkin L.I. Kovredov A.I. Ol'shevskaya V.A. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1981 1775-1777

18. Zakharkin L.I. Kovredov A.I. Ol'shevskaya V.A. Shagumbekova Zh.S. *J. Organometal. Chem.* 1982 **226** 217-222

19. Kovredov A.I. Shaugumbekova Zh.S. Petrovskii P.V. Zakharkin L.I. *J. Gen. Chem. U.S.S.R.* 1989 **59** 537-540

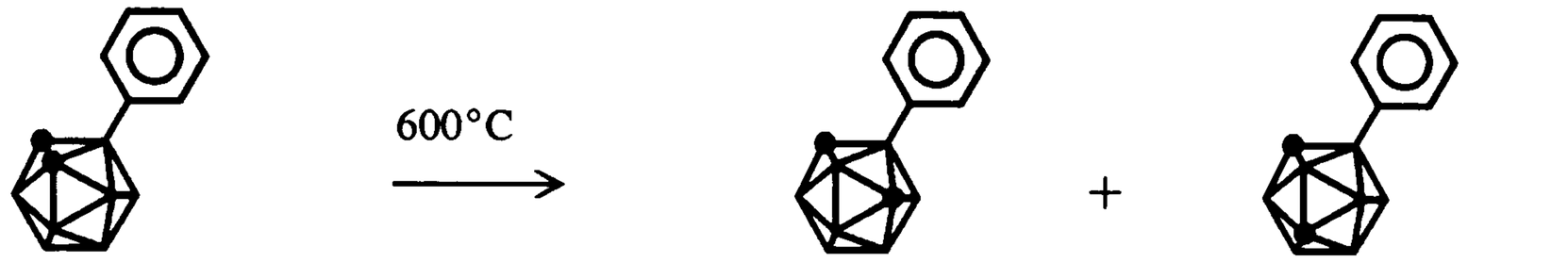
20. Tamao K. Sumitani K. Kiso Y. Zembayashi M. Fujioka A. Kodama S. Nakajima I. Minato A. Kumada M. *Bull. Chem. Soc. Japan* 1976 **49** 1958-1969

21. Zakharkin L.I. Lebedev V.N. Zhigareva G.G. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1984 2208



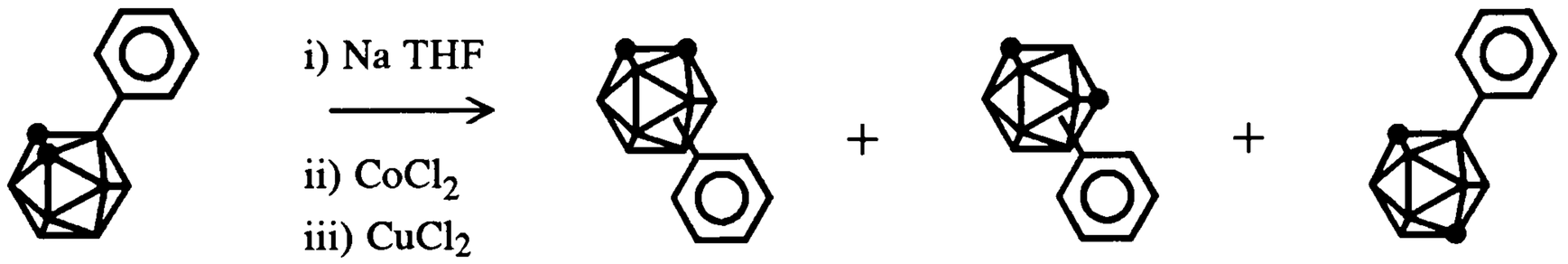
Mechanism of palladium-catalysed 9-phenyl-*ortho*-carborane formation

3-aryl-*ortho*-carborane undergoes thermal rearrangement at 500-600°C in the gas phase to give 2- and 4-aryl-*meta*-carboranes[22,23]. The carboranyl B - aryl C bond is unaffected at these temperatures showing promise for boron-aryl carboranes as monomers in CPEK formation.



$3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{11}$ $2\text{-}C_6H_5\text{-}1,7\text{-}C_2B_{10}H_{11}$ $4\text{-}C_6H_5\text{-}1,7\text{-}C_2B_{10}H_{11}$

A mixture of boron-aryl-*ortho*-, -*meta*- and -*para*-carborane isomers can be produced from 3-aryl-*ortho*-carborane by complexed redox rearrangement[15]. The dianion of the 3-aryl-*ortho*-carborane rearranges in the presence of cobalt chloride and then oxidation by copper chloride gives a mixture of all possible boron-aryl carboranes.



$3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{11}$

3-, 4-, 8- or 9-$C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{11}$ 2-, 4-, 5- or 9-$C_6H_5\text{-}1,7\text{-}C_2B_{10}H_{11}$ $2\text{-}C_6H_5\text{-}1,12\text{-}C_2B_{10}H_{11}$

2- and 4-(4-methylphenyl)-*meta*- and 3-(4-methylphenyl)-*ortho*-carborane can be oxidized by chromium trioxide and sulphuric acid to form their 4-carboxyphenyl analogues[10,14,22,23]. Substitution occurs on the phenyl group of 9-phenyl-*ortho*- and *meta*-carboranes by nitration, acetylation, bromination and mercuration[24]. These reactions, except nitration[25], do not occur on 1- and 3-phenyl-

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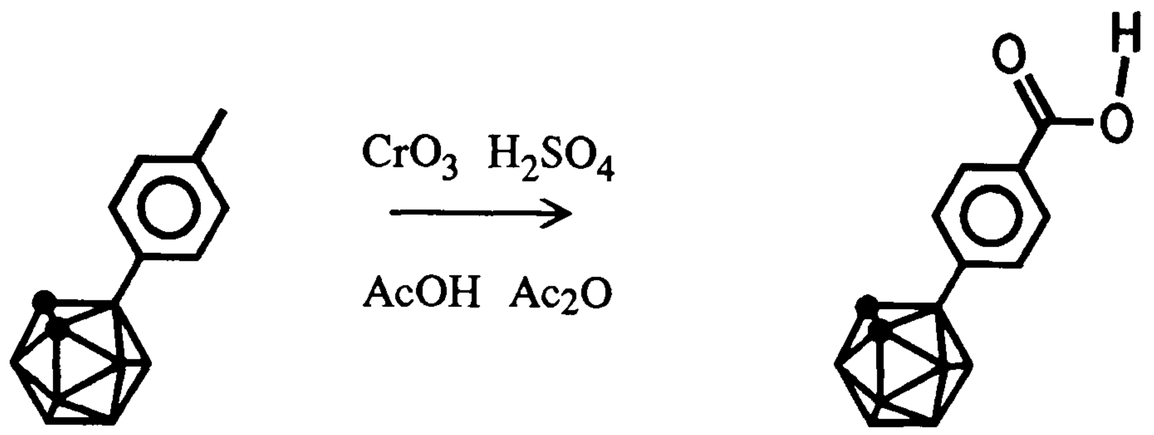
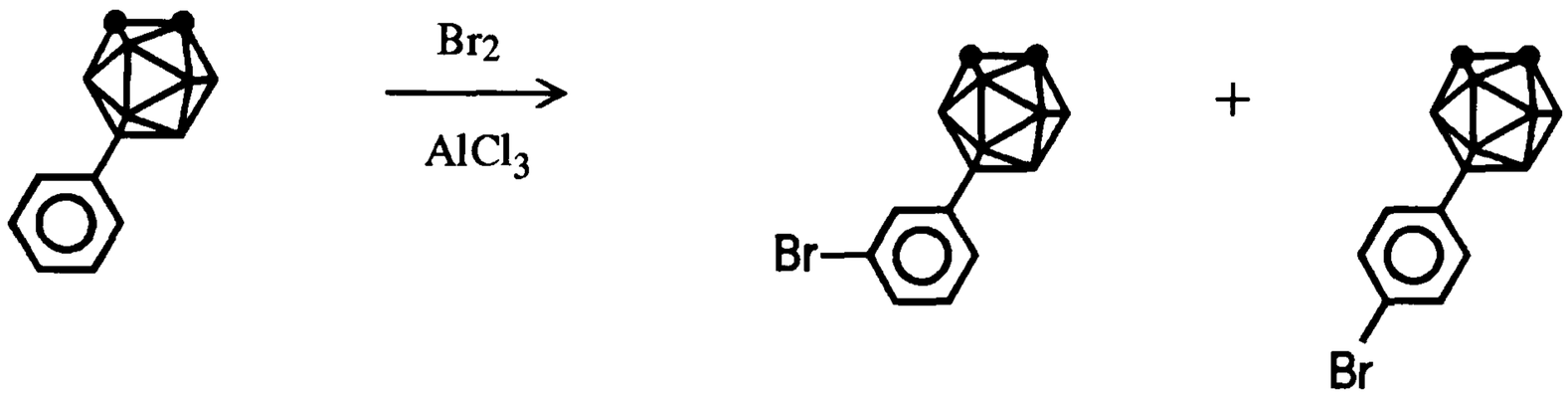
22. Kalinin V.N. Kobel'kova N.I. Zakharkin L.I. *J. Organometal. Chem.* 1979 **172** 391-395
23. Kalinin V.N. Kobel'kova N.I. Zakharkin L.I. *J. Gen. Chem. U.S.S.R.* 1978 **48** 857-858
24. Zakharkin L.I. Ol'shevskaya V.A. Antonovich V.A. *J. Org. Chem. U.S.S.R.* 1987 **23** 1513-1516
25. Zakharkin L.I. Kalinin V.N. Shepilov I.P. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1966 1241

ortho-carborane and 1- and 2-phenyl-*meta*-carborane as the cage acts as an electron-withdrawing substituent if the phenyl group is linked to the carboranyl carbon or the least negatively charged boron atom, i.e. 3-position, whereas it acts as an electron donor if the phenyl group is linked to carboranyl boron at the 9-position.



$3\text{-}(4\text{-}CH_3C_6H_4)\text{-}1,2\text{-}C_2B_{10}H_{11}$ $3\text{-}(4\text{-}HO_2CC_6H_4)\text{-}1,2\text{-}C_2B_{10}H_{11}$



$9\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{11}$ $9\text{-}(3\text{-}BrC_6H_4)\text{-}1,2\text{-}C_2B_{10}H_{11}$ $9\text{-}(4\text{-}BrC_6H_4)\text{-}1,2\text{-}C_2B_{10}H_{11}$

Calculations on the induction constants of *ortho*- and *meta*-carborane using ^{19}F n.m.r. data of fluorophenyl-*ortho*- and *meta*-carboranes showed that the electron-withdrawing properties of the cage depends on the position of the substituent attached to the cage[12,13,14,15,16,17,22].

For *ortho*-carborane, order of increasing cage electron-donation where substituent is attached to position in cage is;

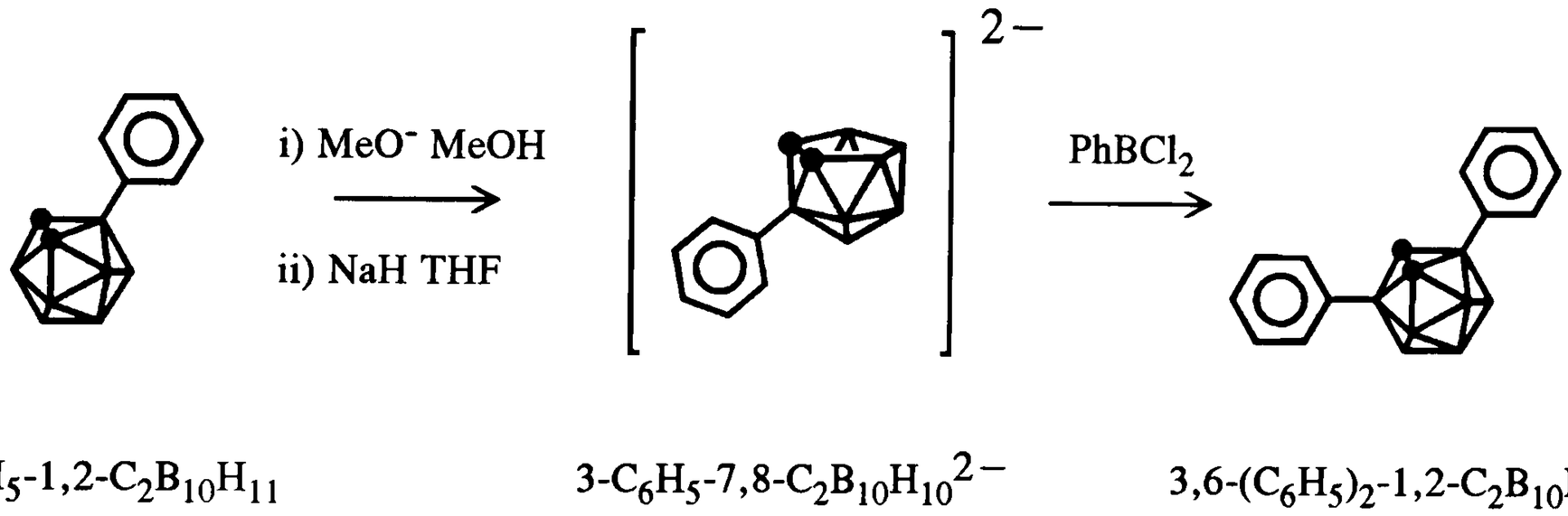
$$1,2 < 3,6 < 4,5,7,11 < (8,10)\ 9,12$$

For *meta*-carborane,

$$1,7 < 2,3 < 4,6,8,11 < (5,12) < 9,10$$

MONOMER SYNTHESES AND MODEL REACTIONS

It was considered that boron-substituted carboranes could act as monomers for CPEK formation. CPEKs produced from these carboranes might have better thermal properties than CPEKs from carboranyl carbon-substituted carborane monomers as carboranyl B - aryl C bond could be stronger than carboranyl C - aryl C bond. The carboranyl C - aryl C bond is cleaved in 1-phenyl-*meta*-carborane at 500°C[26] whereas the carboranyl B - aryl C bond in 3-(4-methylphenyl)-*meta*-carborane is unaffected at 550°C[22]. Bis(4-carboxyphenyl)- and bis(4-phenoxyphenyl)-carboranes with the aryl groups attached to cage boron atoms were considered likely candidates for CPEK formation. 3,6-diaryl-*ortho*-carboranes can be produced from 3-aryl-*ortho*-carboranes via boron insertion using aryl boron dichlorides[11] but 4-methylphenyl and 4-phenoxyphenyl boron dichlorides are difficult to prepare.



$3\text{-}C_6H_5\text{-}1,2\text{-}C_2B_{10}H_{11}$ $3\text{-}C_6H_5\text{-}7,8\text{-}C_2B_{10}H_{10}^{2-}$ $3,6\text{-}(C_6H_5)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$

The palladium-catalysed boron-aryl carborane formation is relatively simple as the reagents required are easily obtained. 9,12-bis(4-phenoxyphenyl)-*ortho*- and 9,12-bis(4-carboxyphenyl)-*ortho*-carborane were targeted as potential monomers for CPEK formation in this study because the starting carborane material, 9,12-diodo-*ortho*-carborane is easily made.

9,12-bis(4-methylphenyl)-*ortho*-carborane (**VII**) was obtained from 9,12-diiodo-*ortho*-carborane and a ten-fold excess of 4-methylphenyl magnesium halide using the air-stable bis(triphenylphosphino)palladium dichloride as catalyst. The product was easily isolated from the reaction mixture as it is sparingly soluble

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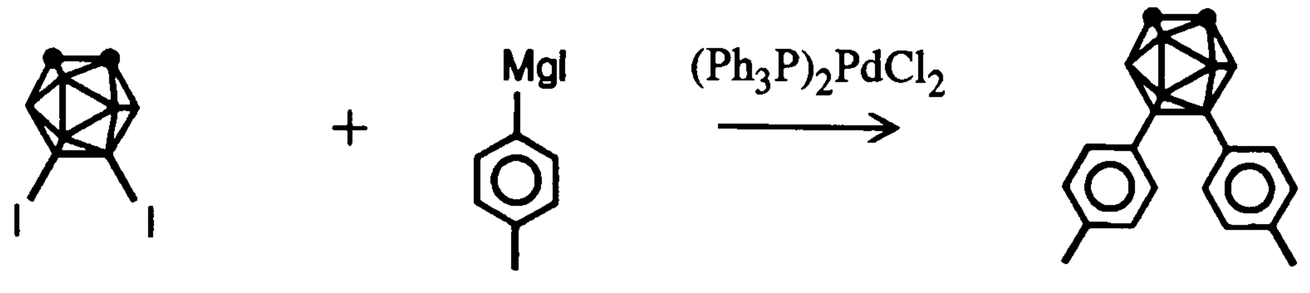
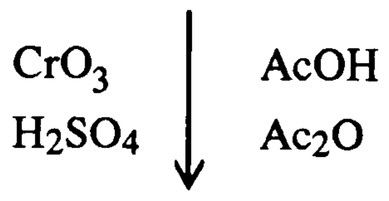
26. Zakharkin L.I. Kalinin V.N. Balykova T.N. Gribkova P.N. Korshak V.V. *J. Gen. Chem. U.S.S.R.* 1973 **43** 2249-2254

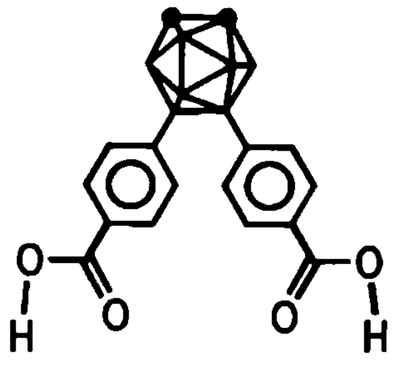
in diethyl ether. The diaryl carborane was oxidized to 9,12-bis(4-carboxyphenyl)-*ortho*-carborane (**VIII**) with chromium trioxide and sulphuric acid.



$9,12\text{-}I_2\text{-}1,2\text{-}C_2B_{10}H_{10}$

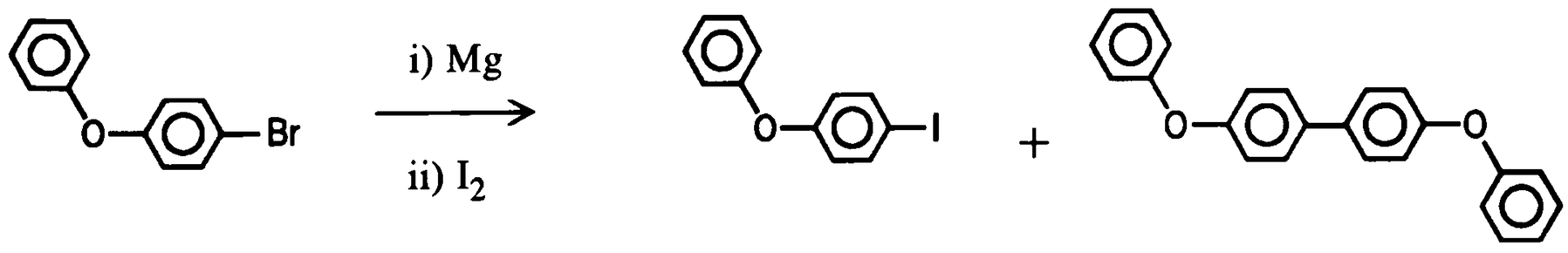
(VII)



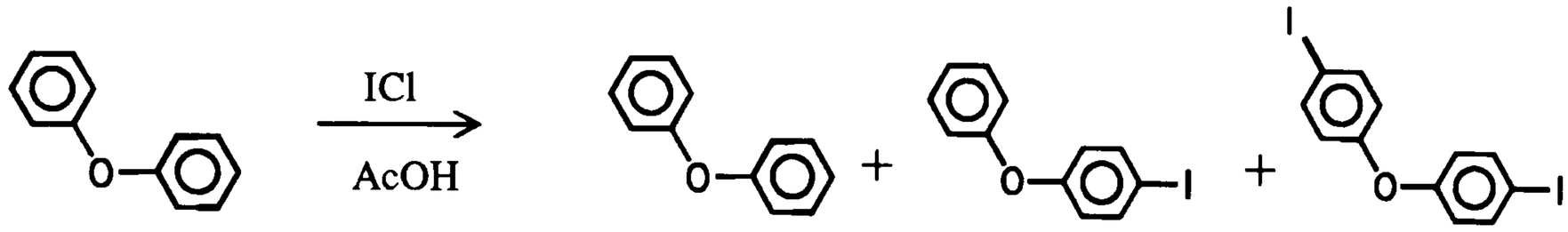


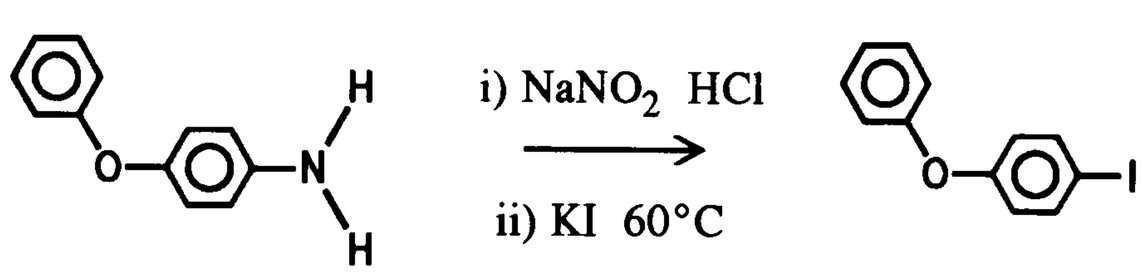
(VIII)

4-iododiphenyl ether, required for the formation of 9,12-bis(4-phenoxyphenyl)-*ortho*-carborane, was made by three different reactions. 4-bromodiphenyl ether was converted to a Grignard reagent with magnesium and the Grignard reagent reacted with iodine to give 4-iododiphenyl ether but 4,4′-diphenoxybiphenyl was also produced in substantial amounts[7c]. Equimolar amounts of iodine monochloride and diphenyl ether in glacial acetic acid gave a mixture of the starting ether, 4-iododiphenyl ether and 4-iodophenyl ether[27]. The best yield of 4-iododiphenyl ether was produced from diazotization of 4-aminodiphenyl ether followed by addition of potassium iodide[28].

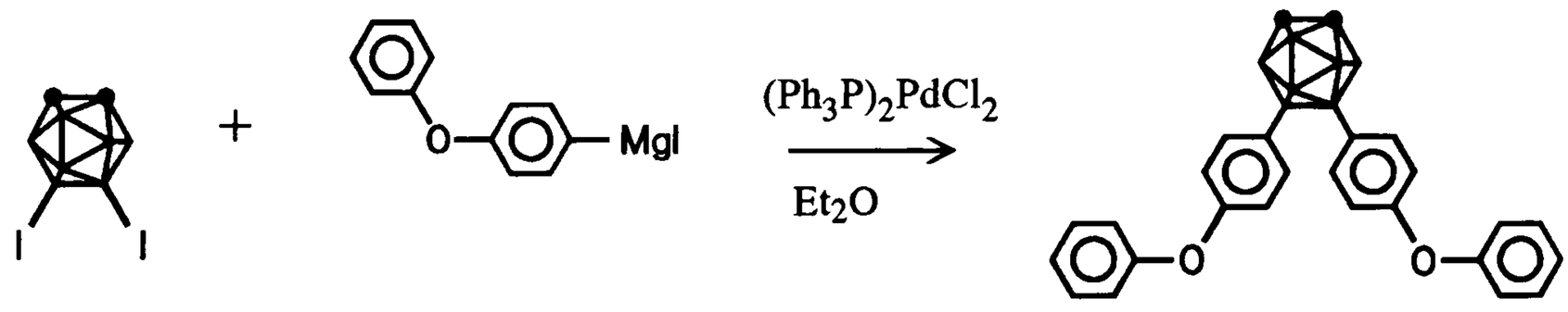


27. Brewster R.Q. Strain F. *J. Am. Chem. Soc.* 1934 **56** 117-120
28. Scarborough H.A. *J. Chem. Soc.* 1929 **132** 2361-2367



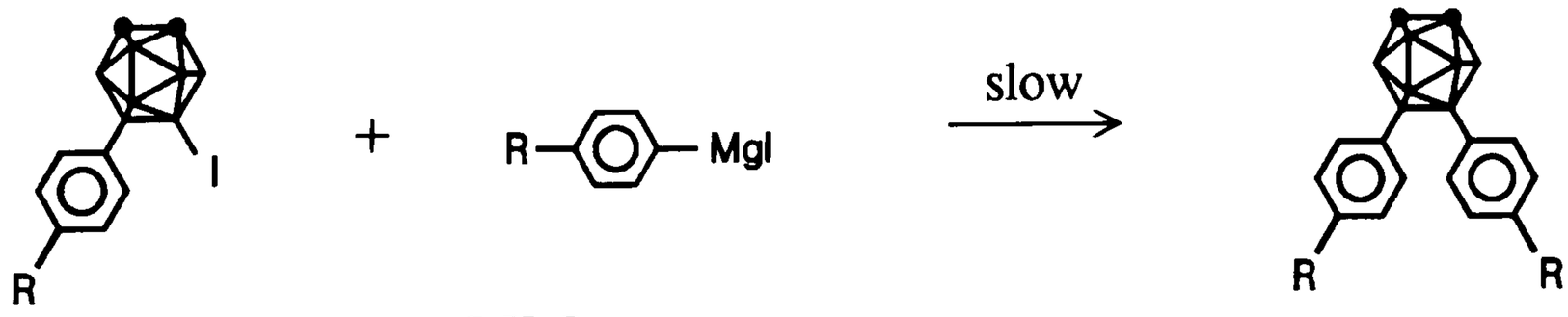


9,12-bis(4-phenoxyphenyl)-*ortho*-carborane (**IX**) was obtained from 9,12-diiodo-*ortho*-carborane and a ten-fold excess of 4-phenoxyphenyl magnesium iodide in diethyl ether with refluxing. The yields of 9,12-diaryl-*ortho*-carboranes produced from 9,12-diiodo-*ortho*-carborane are only 28-32% which could be explained by the steric effect from the aryl group on the second iodine to be displaced. Oxidation of 9,12-dimethyl-*ortho*-carborane gave only the monocarboxylic acid, 9-methyl-12-carboxy-*ortho*-carborane, which is also explained by the steric effect of the carboxylic group on the second reaction site[29].



(IX)

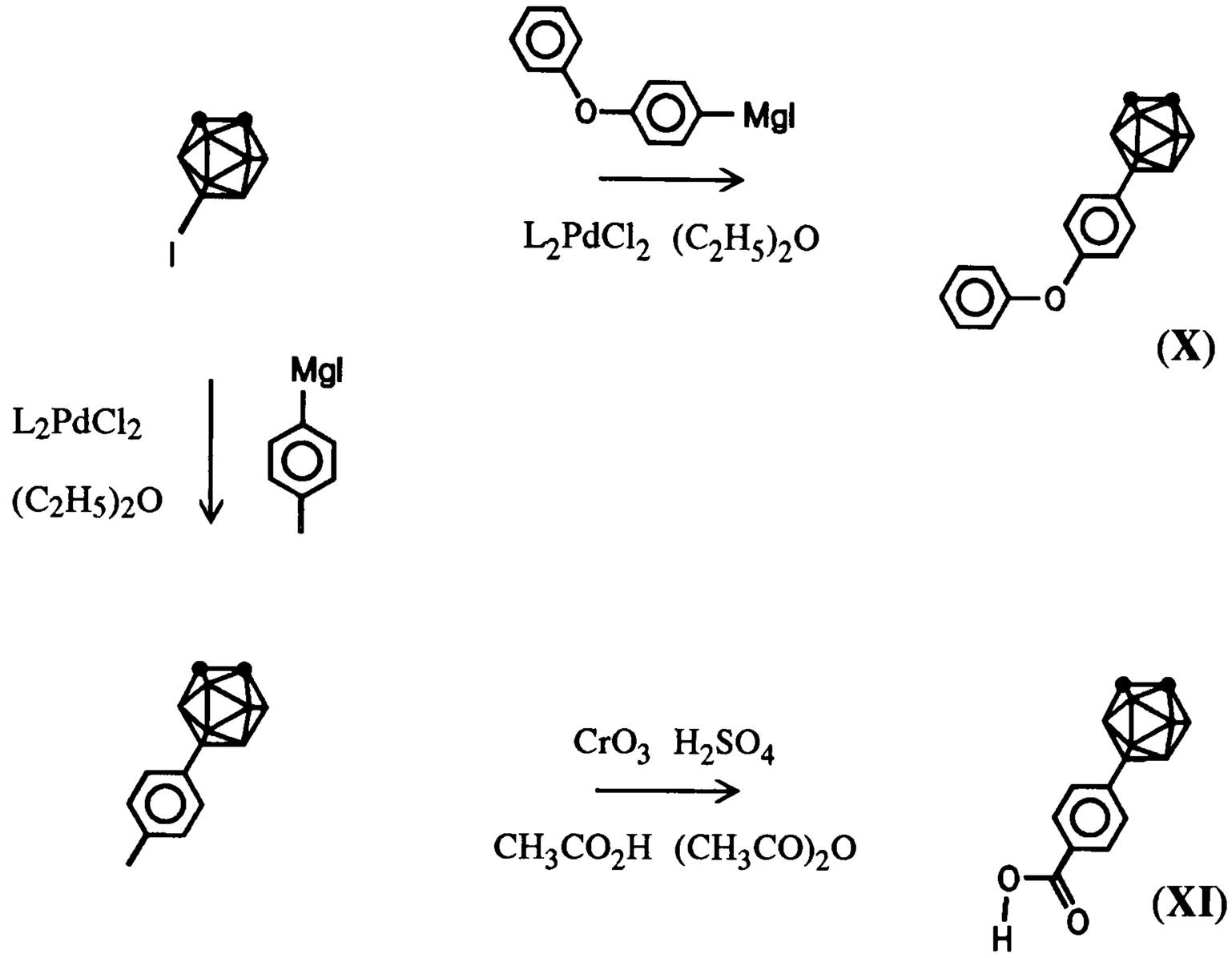
Rate determining step of 9,12-diaryl-*ortho*-carborane formation



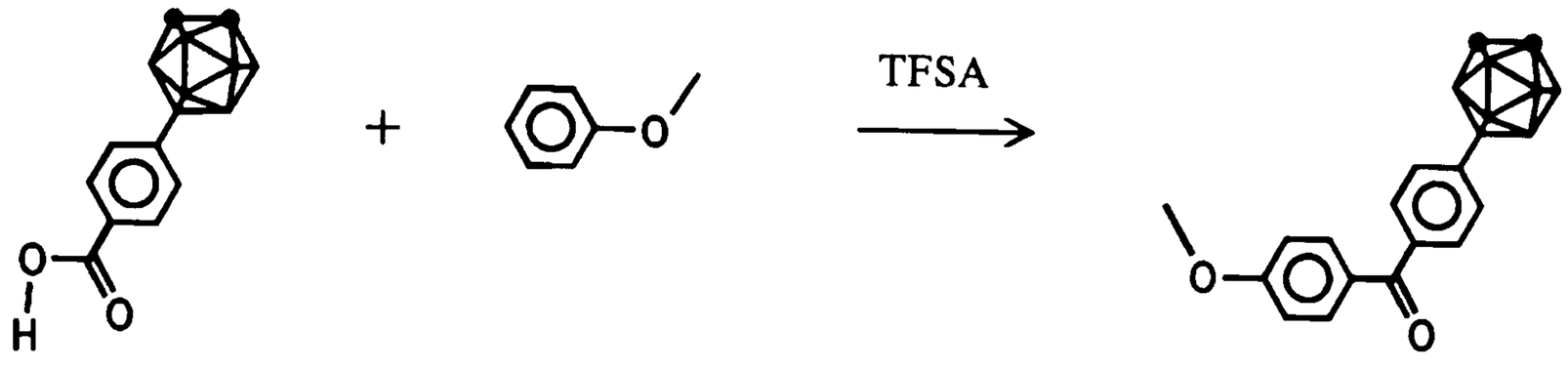
R = CH_3, C_6H_5O

29. Zakharkin L.I. Kovredov A.I. Ol'shevskaya V.A. Antonovich V.A. *J. Organometal. Chem.* 1984 **267** 81-91

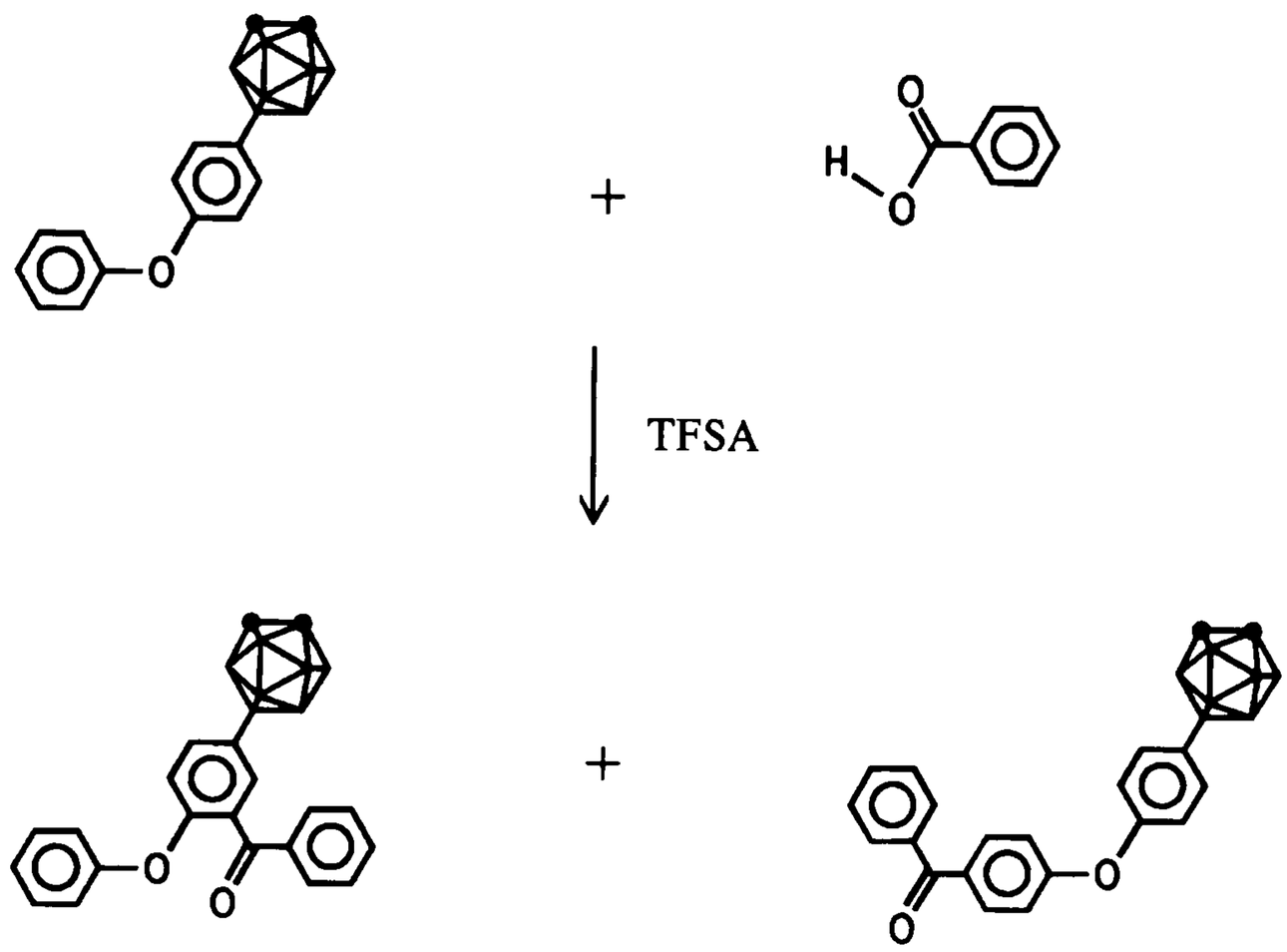
To determine the suitability of these diaryl carboranes produced for CPEK formation, 9-(4-phenoxyphenyl)-*ortho*-carborane (**X**) and 9-(4-carboxyphenyl)-*ortho*-carborane (**XI**) were also made, via similar routes as for their diaryl carborane analogues, from 9-iodo-*ortho*-carborane.



9-(4-carboxyphenyl)-*ortho*-carborane and anisole in TFSA gave the expected product 9-(4-methoxy-4-benzoylphenyl)-*ortho*-carborane (**XII**) according to ^{13}C n.m.r. data. However 9-(4-phenoxyphenyl)-*ortho*-carborane and benzoic acid in TFSA gave two carborane containing compounds which could not be separated by column chromatography. Infrared, mass spectroscopy and elemental analysis of the mixture point to both compounds containing a molecular formula $C_{21}H_{24}B_{10}O_2$, with ether and ketone links. The ^{13}C n.m.r. spectrum of the mixture gave at least twenty peaks in the aromatic region 140-110ppm and three peaks in the carboranyl region 55-45ppm which indicate 9-(3-benzoyl-4-phenoxyphenyl)-*ortho*-carborane (**XIII**) and 9-(4′-benzoyl-4-phenoxyphenyl)-*ortho*-carborane (**XIV**) could be present in approximately equal amounts. The latter product is produced by electrophilic attack on the benzene ring attached to the cage as the cage is electron-donating.

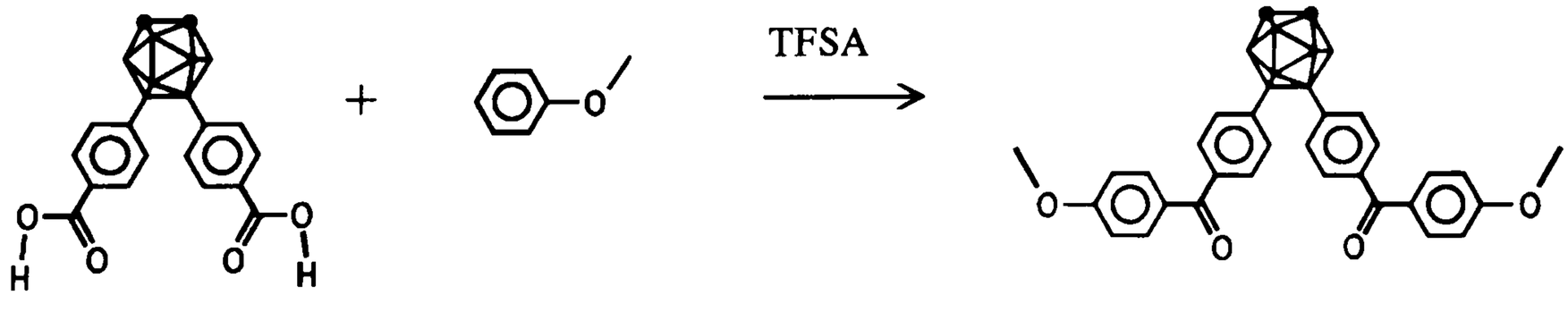


(XII)



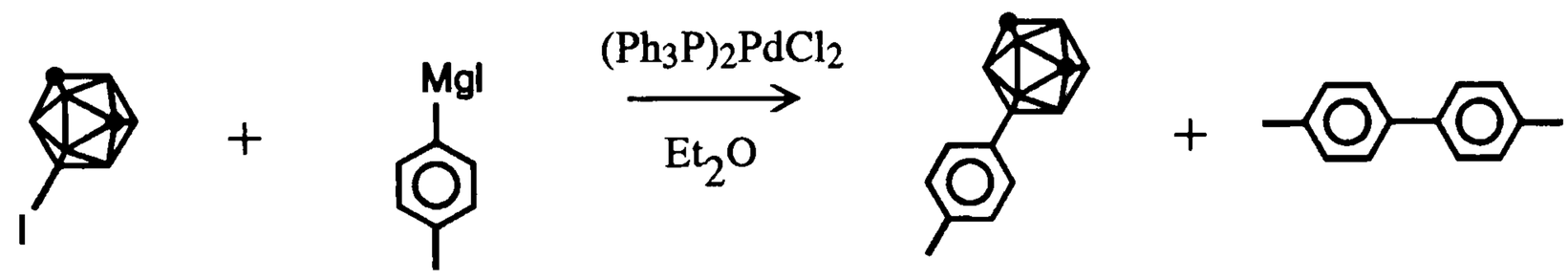
(XIII) **(XIV)**

From these model reactions 9,12-bis(4-carboxyphenyl)-*ortho*-carborane seems to have suitable monomer properties for CPEK formation. The potential carborane monomer gave the expected product 9,12-bis(4-methoxy-4-benzoylphenyl)-*ortho*-carborane (**XV**) with two molecular proportions of anisole in TFSA.



(XV)

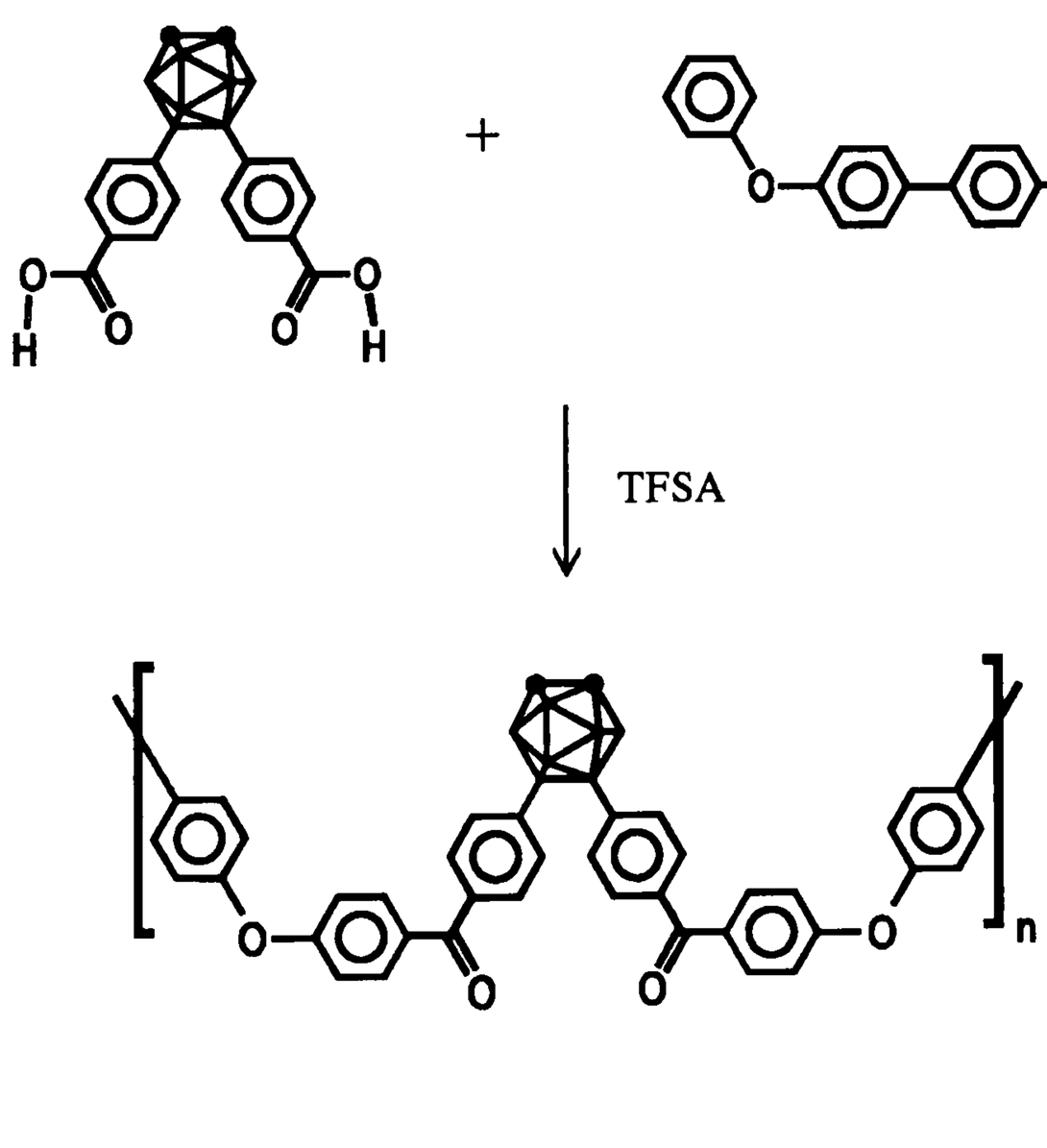
9,10-bis(4-carboxyphenyl)-*meta*-carborane could also be a suitable monomer for CPEK formation. The reaction between 9-iodo-*meta*-carborane and 4-methylphenyl magnesium iodide with catalyst gave a low yield of 9-(4-methylphenyl)-*meta*-carborane (**XVI**). Synthesis of 9,10-bis(4-methylphenyl)-*meta*-carborane was not attempted as the yield from 9,10-diiodo-*meta*-carborane is expected to be very low due to steric effect on the second reaction site by the aryl group.



(XVI)

CONCLUSIONS AND FUTURE WORK

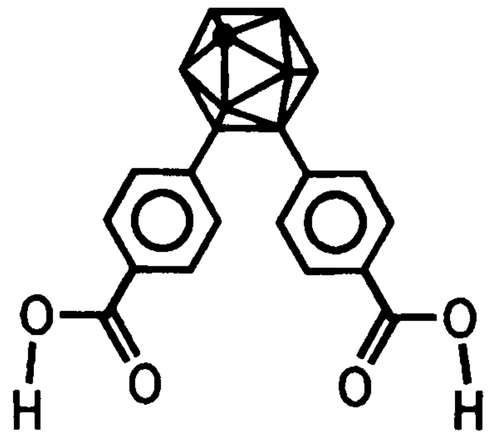
9,12-bis(4-carboxyphenyl)- and 9,12-bis(4-phenoxyphenyl)-*ortho*-carborane were successfully synthesised from 9,12-diiodo-*ortho*-carborane as the carborane precursor. 9-(4-phenoxyphenyl)-*ortho*-carborane and benzoic acid in TFSA gave two products which eliminates 9,12-bis(4-phenoxyphenyl)-*ortho*-carborane as a suitable monomer for CPEK formation. The carborane diacid however is, according to model reactions, suitable for CPEK formation. A CPEK containing carboranyl boron - aryl carbon links is expected to form from 9,12-bis(4-carboxyphenyl)-*ortho*-carborane and a suitable aromatic ether like 4,4-diphenoxybiphenyl in TFSA. 9,12-bis(4-carboxyphenyl)-*ortho*-carborane could also be used to form high temperature polyamides and polyesters with aromatic diamines and bisphenols respectively.



Possible CPEK formation

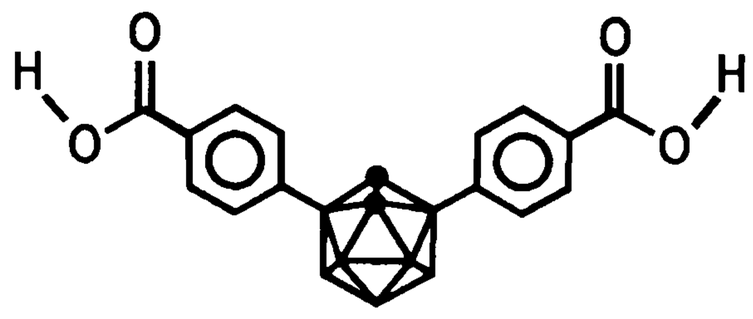
The yields of the boron-aryl carboranes produced in this study could be improved by a change in experimental procedure. A recent modified method uses benzene as co-solvent to speed up the reaction and butyllithium to separate the carboranes from the biaryl side products[19].

9,10-bis(4-carboxyphenyl)-*meta*-carborane (**XVII**) as a monomer for CPEK formation has the advantage of a more thermally stable carborane cage than its *ortho*-carborane analogue but the synthesis of the *meta* derivative requires more severe conditions than its *ortho* analogue.

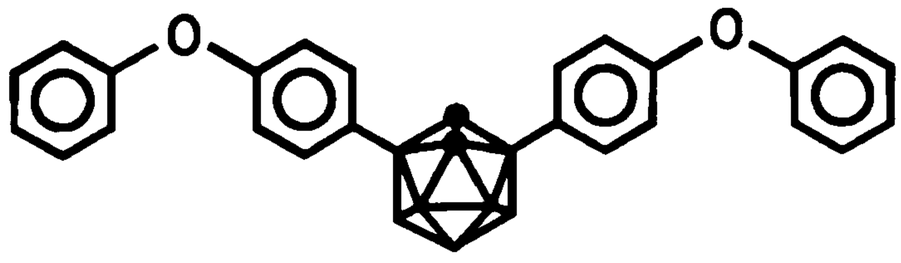


(XVII)

3,6-bis(4-carboxyphenyl)- (**XVIII**) and 3,6-bis(4-phenoxyphenyl)-*ortho*-carborane may also be suitable monomers for CPEK formation. The 3,6-bis(4-phenoxyphenyl)-*ortho*-carborane (**XIX**), unlike the 9,12-substituted analogue, with the cage as an electron-acceptor could form a single product with excess benzoic acid in TFSA.



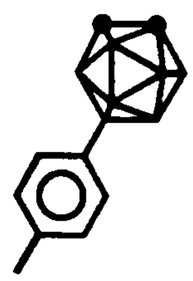
(XVIII)



(XIX)

EXPERIMENTAL SECTION

9-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

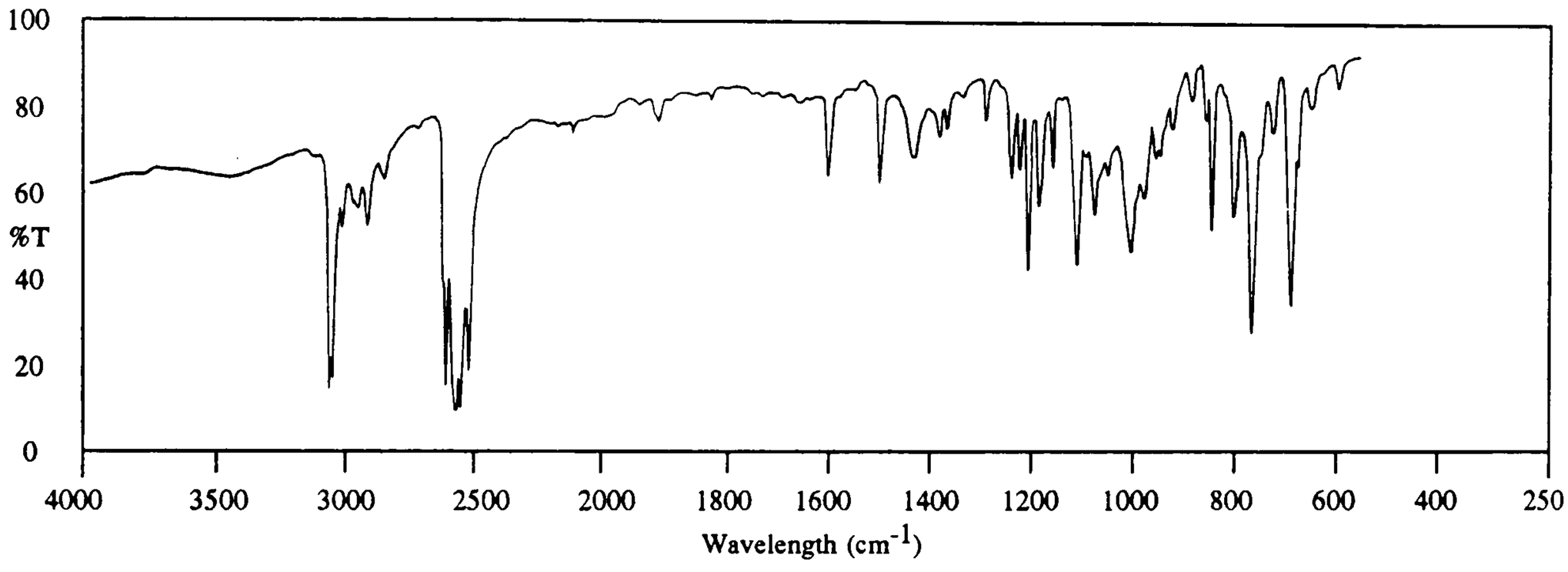


A solution of 8.72g (0.04 moles) 4-iodotoluene in 20ml dry diethyl ether was added dropwise to 1.5g (0.06 moles) of magnesium filings in 20ml anhydrous diethyl ether at 0°C under nitrogen. After reaction, the excess filings were filtered off under nitrogen and the filtrate was added to a solution of 2.70g (0.01 moles) of 9-iodo-*ortho*-carborane and 0.04g (0.0568 mmoles) of bis(triphenylphosphino)palladium dichloride in 30ml diethyl ether. The solution was refluxed under nitrogen for 24 hours. After cooling, the black mixture was decomposed with 100ml of distilled water and the organic layer was washed with two 30ml portions each of hydrochloric acid and distilled water. The organic layer was dried over anhydrous magnesium sulphate, filtered and the ether was pumped off. The residue was fractionally sublimed at 0.01mmHg to give 2.1g of pure 4,4′-dimethylbiphenyl at 120°C and 1.1g (47%) of 9-(4-methylphenyl)-*ortho*-carborane at 160°C. The latter compound was recrystallized from hexane.

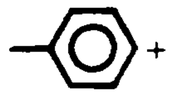
Melting point = 127-128°C (lit[18]. = 129-129.5°C)

Analysis Found: C,45.8; H,8.0. $C_9H_{18}B_{10}$ requires C,46.2; H,7.7.

Infrared (KBr disc; cm^{-1}) 3055(s), 3051(s), 3012(m), 2974(w), 2952(w), 2914(w), 2855(w), 2622(s), 2582(s), 2570(s), 2539(s), 1602(s), 1507(m), 1500(w), 1441(m), 1393(w), 1381(w), 1310(w), 1259(w), 1242(w), 1228(m), 1209(m), 1184(w), 1136(m), 1105(w), 1031(m), 1005(w), 973(w) 952(w), 915(w), 888(w), 878(m), 838(m), 831(m), 801(s), 782(w), 759(w), 726(s), 712(m), 690(w), 638(w), 570(w), 540(w), 529(w), 499(m).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 236 corresponding to the species $^{12}C_9{}^{1}H_{18}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 230 and 236. A peak of m/e 91 was also present assigned to $C_7H_7{}^{+}$, i.e.:

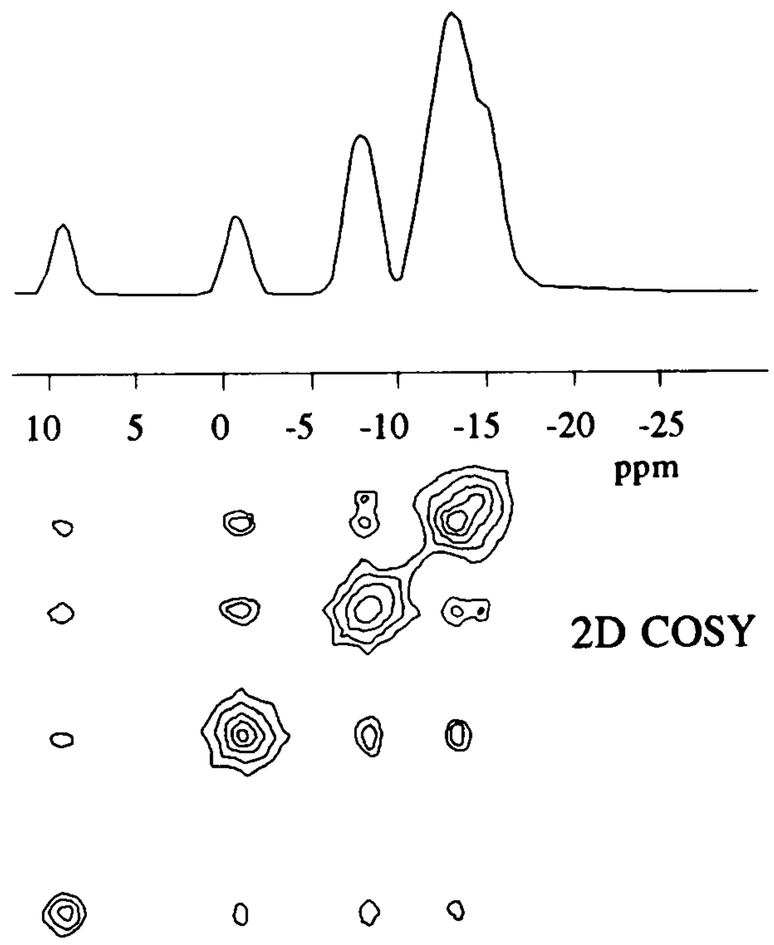


^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.59 7.56 7.05 7.02	4	doublet of doublets	aromatic C(c,d)-H
2.12	3	singlet	methyl C(a)-H
2.08	1	broad singlet	carboranyl C(g)-H
1.98	1	broad singlet	carboranyl C(f)-H
3.9-1.1	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent C_6D_6, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

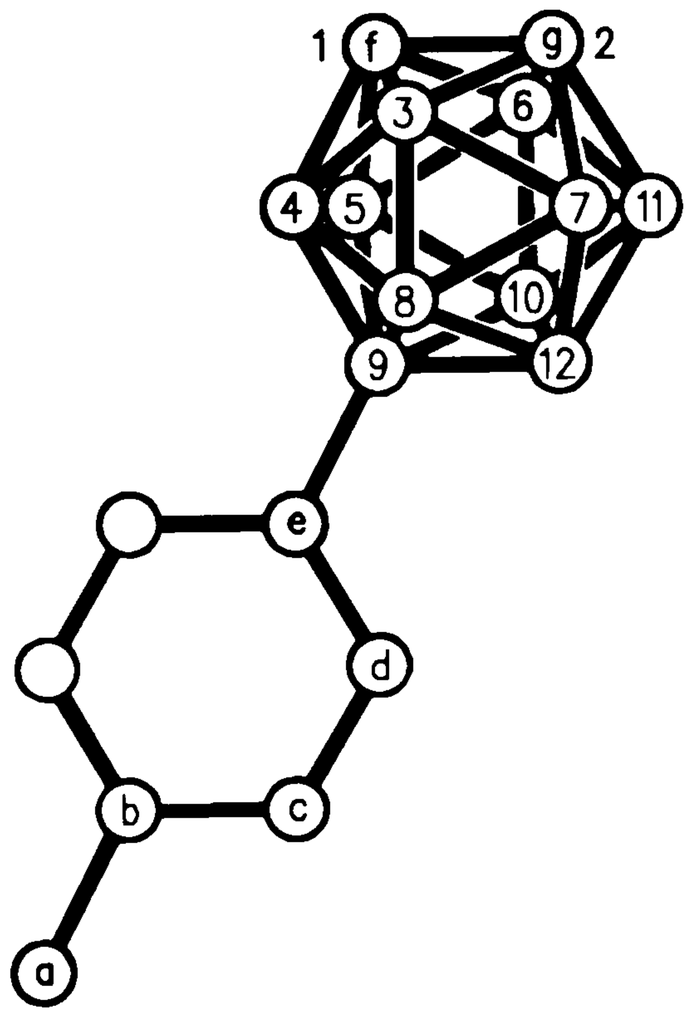
δ_{ppm}	intensity	position of boron
8.81	1	9
-1.42	1	12
-7.88	2	8,10
-13.21	4	4,5,7,11
-14.10	2	3,6



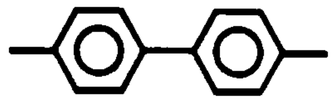
2D COSY

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
136.92	b
132.35	d
128.28	c
53.10	f
48.65	g
21.18	a



4,4′-dimethylbiphenyl



Melting point = 118-120°C (lit[30]. = 117-119°C)

Analysis Found: C,92.1; H,7.7. $C_{14}H_{14}$ requires C,92.3; H,7.7.

Infrared (KBr disc; cm^{-1}) 3059(w), 3032(w), 2972(w), 2952(w), 2922(w), 2862(w), 1925(w), 1910(w), 1729(w), 1612(w), 1564(w), 1543(w), 1505(s), 1489(m), 1451(w), 1404(w), 1388(w), 1374(w), 1328(w), 1314(w), 1262(w), 1212(w), 1180(w), 1151(w), 1123(w), 1113(w), 1039(w), 1031(w), 1008(w), 962(w), 940(w), 848(w), 841(w), 837(w), 808(s), 803(s), 726(w), 710(w), 542(w), 514(w), 502(m), 498(m), 422(w).

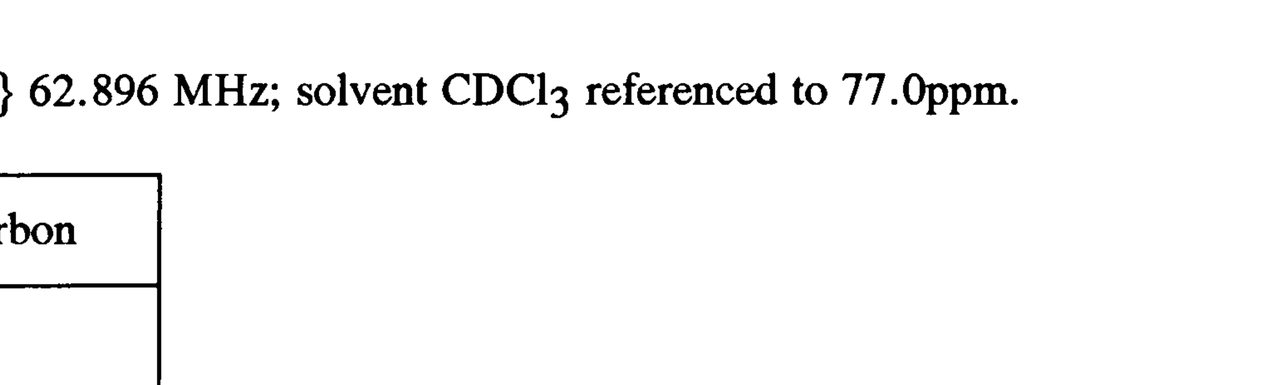
Mass spectrum (E.I.) A highest mass peak was observed at m/e 182 corresponding to the species $^{12}C_{14}{}^{1}H_{14}$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.53 7.50 7.29 7.26	8	doublet of doublets	aromatic C(c,d)-H
2.36	6	singlet	methyl C(a)-H

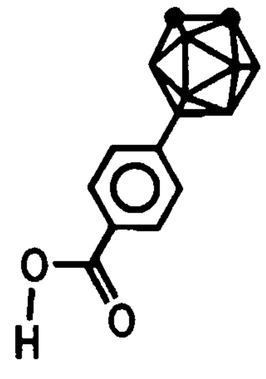
^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
138.30	b
136.65	e
129.41	d
126.78	c
21.04	a



30. Gardner J. Borgstrom P. *J. Am. Chem. Soc.* 1929 **51** 3375-3377

9-(4-carboxyphenyl)-1,2-dicarba-*closo*-dodecaborane

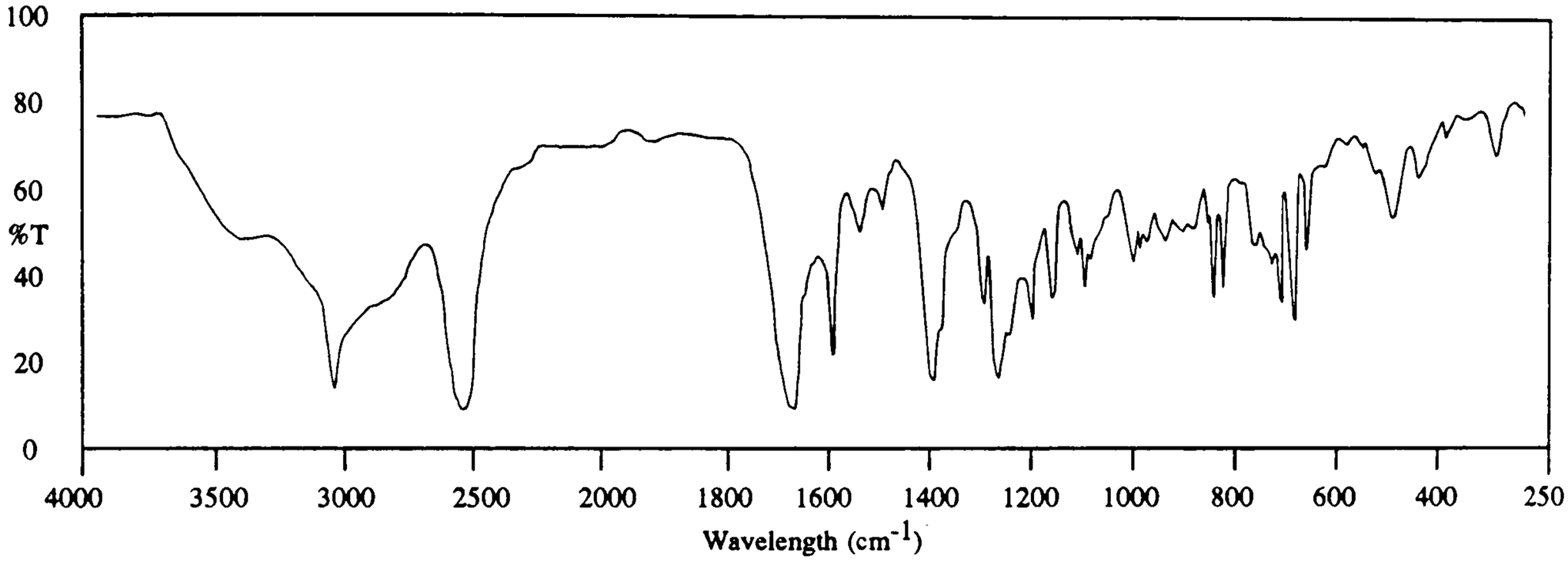


3g (30 mmoles) of chromium (IV) trioxide was gradually added to a stirred solution of 0.47g (2 mmoles) 9-(4-methylphenyl)-*ortho*-carborane, 7.5ml acetic anhydride and 1.5ml concentrated sulphuric acid in 30ml glacial acetic acid at 20°C. After two hours the green mixture was poured into 250ml cold water. The precipitate formed was filtered off, washed with distilled water and dried *in vacuo*. 0.40g (75.5%) 9-(4-carboxyphenyl)-*ortho*-carborane was obtained as white powder.

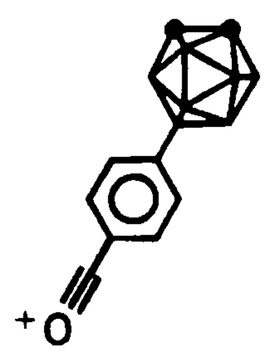
Melting point = 251-252°C

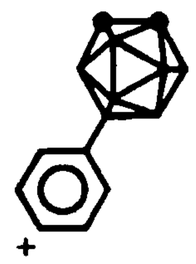
Analysis Found: C,40.2; H,6.1. $C_9H_{16}B_{10}O_2$ requires C,40.9; H,6.1.

Infrared (KBr disc; cm^{-1}) 3666-2310(m,br), 3060(s), 2582(s), 1676(s), 1602(s), 1550(w), 1503(w), 1414(s), 1398(m), 1315(m), 1291(s), 1270(m), 1187(m), 1137(w), 1123(m), 1111(w), 1031(m), 1019(w), 1006(w), 972(w), 934(w), 915(w), 888(w), 879(m), 861(m), 800(w), 768(m), 752(m), 728(m), 699(w), 565(w), 534(m), 482(w), 469(w), 428(w), 331(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 266 corresponding to the species $^{12}C_9{}^{1}H_{16}{}^{11}B_{10}{}^{16}O_2$, accompanied by the usual carborane isotope distribution pattern between m/e 260 and 266. Two other groups of peaks were observed at m/e 243-249 and 215-221 assigned respectively to:





^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.91 7.88 7.49 7.46	4	doublets of doublet	aromatic C(c,d)-H
4.67	1	broad singlet	carboranyl C(g)-H
4.60	1	broad singlet	carboranyl C(f)-H
4.0-0.8	9	broad multiplet	carboranyl B-H

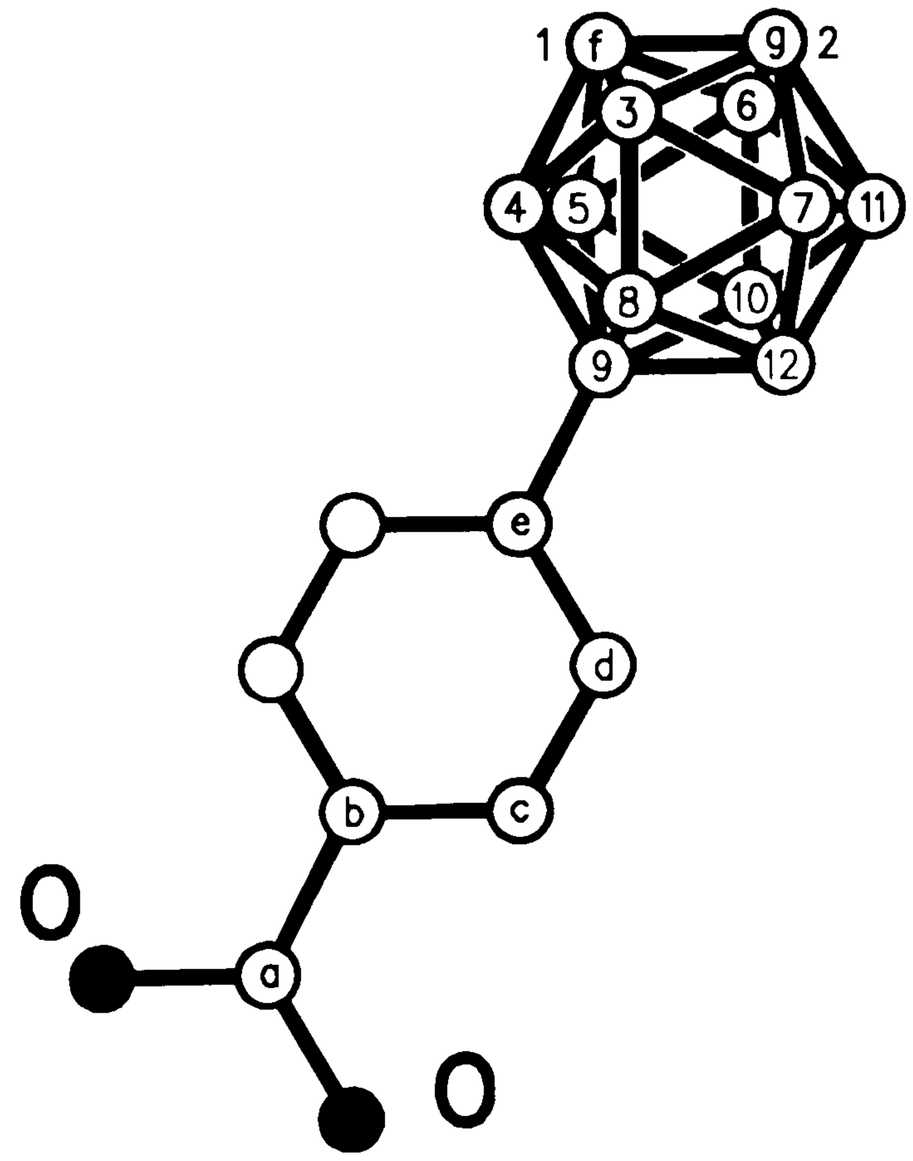
The carboxylic proton peak is not observed between -1 and 20ppm

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

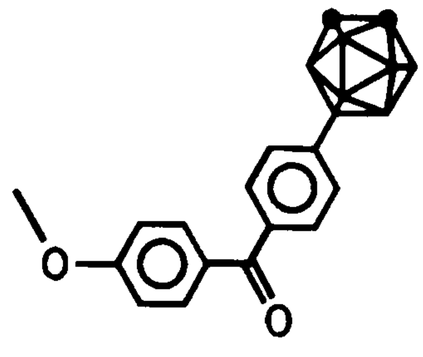
δ_{ppm}	intensity	position of boron
7.00	1	9
-2.09	1	12
-8.42	2	8,10
-13.66	4	4,5,7,11
-14.42	2	3,6

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$ referenced to 28.0ppm.

δ_{ppm}	position of carbon
167.40	a
132.40	b
131.58	d
127.76	c
53.89	f
49.95	g



9-(4′-methoxy-4-benzoylphenyl)-1,2-dicarba-*closo*-dodecaborane

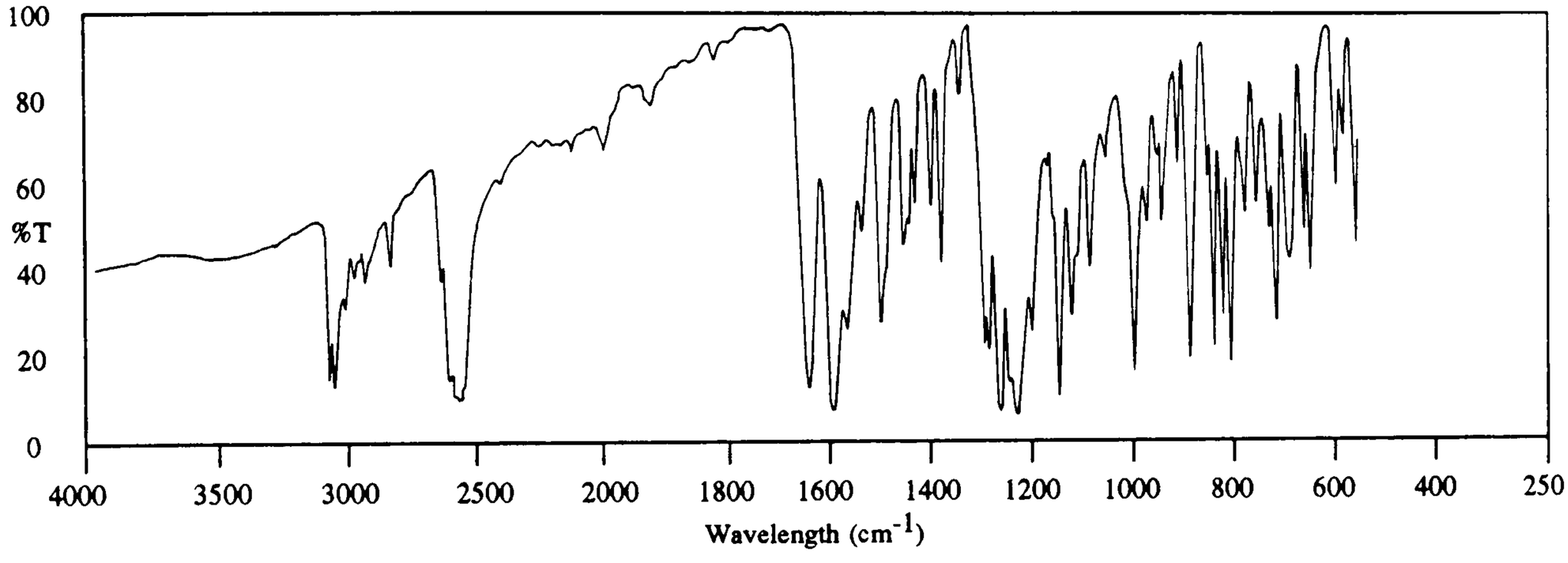


0.264g (1 mmole) 9-(4-carboxyphenyl)-*ortho*-carborane and 0.12g (1.1 mmoles) anisole were dissolved in 3ml of TFSA and left to stand for 24 hours under nitrogen. The dark red solution was poured into water giving a white precipitate which was extracted into diethyl ether. The ether extracts were washed with 10% sodium hydroxide, water, dried over anhydrous magnesium sulphate and filtered. The diethyl ether was removed under reduced pressure leaving a solid which was recrystallized from hexane to give 0.23g (65.0%) of 9-(4′-methoxy-4-benzoylphenyl)-*ortho*-carborane.

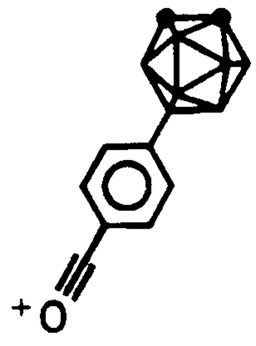
Melting point = 159-160°C

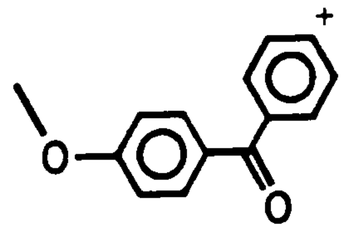
Analysis Found: C,55.0; H,6.2. $C_{16}H_{22}B_{10}O_2$ requires C,54.2; H,6.2.

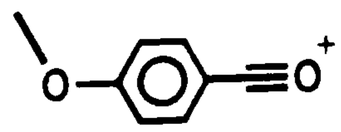
Infrared (KBr disc; cm^{-1}) 3064(m), 3048(m), 3007(w), 2972(w), 2957(w), 2933(w), 2914(w), 2838(w), 2651(m), 2620(s), 2598(s), 2585(s), 2577(s), 2162(w), 2048(w), 1938(w), 1642(s), 1596(s), 1570(s), 1542(m), 1508(m), 1501(m), 1462(m), 1453(m), 1440(w), 1412(w), 1392(m), 1358(w), 1312(s), 1304(s), 1285(s), 1267(s), 1253(s), 1224(s), 1192(w), 1174(s), 1150(m), 1142(m), 1115(m), 1084(w), 1032(s), 1008(m), 988(w), 978(m), 948(w), 927(s), 889(w), 879(s), 861(m), 848(s), 818(w), 796(w), 772(w), 759(m), 732(m), 705(w), 691(m), 641(w), 628(w), 607(m), 563(w), 552(w), 507(w), 471(w), 421(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 356 corresponding to the species $^{12}C_{16}{}^{1}H_{22}{}^{11}B_{10}{}^{16}O_2$, accompanied by the usual carborane isotope distribution pattern between m/e 350 and 356. Peaks seen at m/e 243-249, 211 and 135 were assigned respectively to:







^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

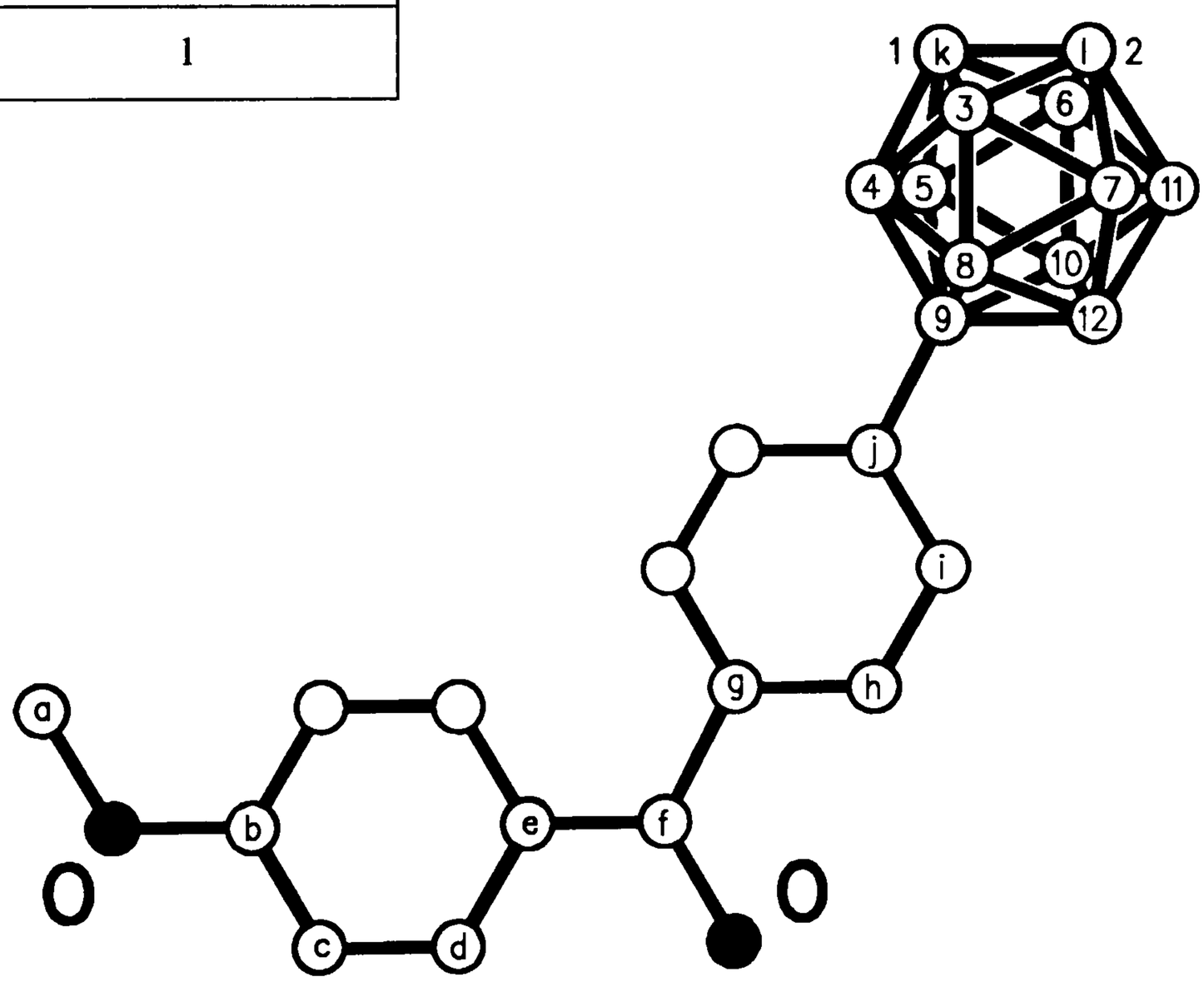
δ_{ppm}	intensity	type of peak	position of proton
7.83 7.79 6.62 6.59	4	doublet of doublets	aromatic C(c,d)-H
7.79 7.76 7.66 7.63	4	doublet of doublets	aromatic C(h,i)-H
3.16	3	singlet	methyl C(a)-H
2.20	1	broad singlet	carboranyl C(l)-H
2.10	1	broad singlet	carboranyl C(k)-H
4.0-0.9	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

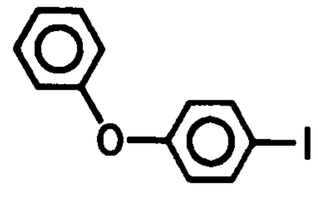
δ_{ppm}	intensity	position of boron
8.17	1	9
-0.81	1	12
-7.35	2	8,10
-12.84	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
195.71	f
165.83	b
136.80	e
132.39	d
132.12	h
130.32	g
128.59	i
113.35	c
55.37	a
53.34	k
49.52	l



Preparations of 4-iododiphenyl ether.



METHOD A

12.5g (0.05 moles) 4-bromophenyl ether in 25ml dry tetrahydrofuran was added dropwise to a refluxing mixture of 3.65g (0.075 moles) magnesium turnings and 25ml dry tetrahydrofuran under a nitrogen atmosphere. After refluxing for four hours, the brown solution was cooled, filtered and treated dropwise to 13.0g (0.051 moles) iodine in 60ml dry tetrahydrofuran. The mixture was refluxed for two hours, cooled and slowly treated with 50ml of distilled water. The product was extracted with three 25ml portions of diethyl ether and the combined ether extracts were washed with 10% sodium thiosulphate and distilled water. The organic mixture was dried over anhydrous magnesium sulphate, filtered and the solvents were removed by rotary evaporator and *in vacuo*. The residue was recrystallized from methanol to give 5.6g (37.8%) of the expected 4-iododiphenyl ether and the mother liqour was concentrated to yield 4.1g (48.5%) of 4,4′-diphenoxybiphenyl.

METHOD B

8.12g (0.05 moles) iodine monochloride was added to a stirred solution of 8.5g (0.05 moles) diphenyl ether in 50ml glacial acetic acid. After 6 hours stirring at 70°C, the dark solution was cooled, poured into 300ml distilled water and decolorized with potassium hydrogen sulphite. Two 30ml portions of diethyl ether were used to extract the organic products and the combined ether extracts were dried over anhydrous magnesium sulphate and filtered and the ether was driven off using a rotary evaporator. The residue was found by thin layer chromatography on silica (with toluene as eluent) to contain three products. It was dissolved in methanol and 3.5g (16.6%) of 4,4′-diiododiphenyl ether was obtained

as crystals. The mother liquor was concentrated to yield 9.8g (66.2%) of the expected 4-iododiphenyl ether. The methanol solution was then vacuum distilled to give 1.2g (14.1%) of unreacted diethyl ether.

METHOD C

18.5g (0.1 moles) of 4-phenoxyaniline was grounded to a powder and dissolved in 150ml of 10% dilute sulphuric acid at 100°C. After cooling the suspension to 0°C with an ice bath and addition of 50g of ice, 7.0g (0.101 moles) of sodium nitrite in 30ml of distilled water was added dropwise at 0-5°C to the solution with stirring. After one hour the solution was filtered to remove impurities and added slowly to a stirred solution of 32g potassium iodide in 50ml water at 60°C. After gas evolution ceased, the mixture was cooled and potassium bisulphide was added in 0.1g portions until the purple colour disappeared. The dark product was extracted with two 50ml portions of diethyl ether and the organic layer was washed with two 25ml portions each of 10% potassium hydroxide, dilute hydrochloric acid and water. The layer was dried over anhydrous magnesium sulphate and filtered. The ether was then pumped off by rotary evaporator leaving a wet amber solid which was recrystallized from methanol to give 23.1g (78.0%) of 4-iododiphenyl ether.

4-iododiphenyl ether

Melting point = 46-47°C (lit[27]. = 48°C)

Analysis Found: C,48.7; H,3.1. $C_{12}H_9IO$ requires C,48.7; H,3.0.

Infrared (KBr disc; cm^{-1}) 3085(w), 3065(w), 3042(w), 1951(w), 1891(w), 1875(w), 1738(w), 1640(w), 1600(m), 1592(m), 1582(m), 1573(m), 1564(w), 1542(w), 1490(s), 1480(s), 1477(s), 1457(m), 1434(w), 1427(w), 1397(w), 1360(w), 1344(w), 1336(w), 1310(w), 1300(m), 1278(s), 1253(s), 1248(s), 1241(s), 1195(m), 1168(s), 1162(s), 1153(m), 1104(w), 1096(w), 1071(m), 1058(m), 1022(m), 1002(m), 963(w), 949(w), 905(w), 871(m), 842(w), 820(s), 786(m), 752(s), 688(m), 638(w), 625(w), 606(w), 599(w), 578(w), 492(m), 489(m), 476(m).

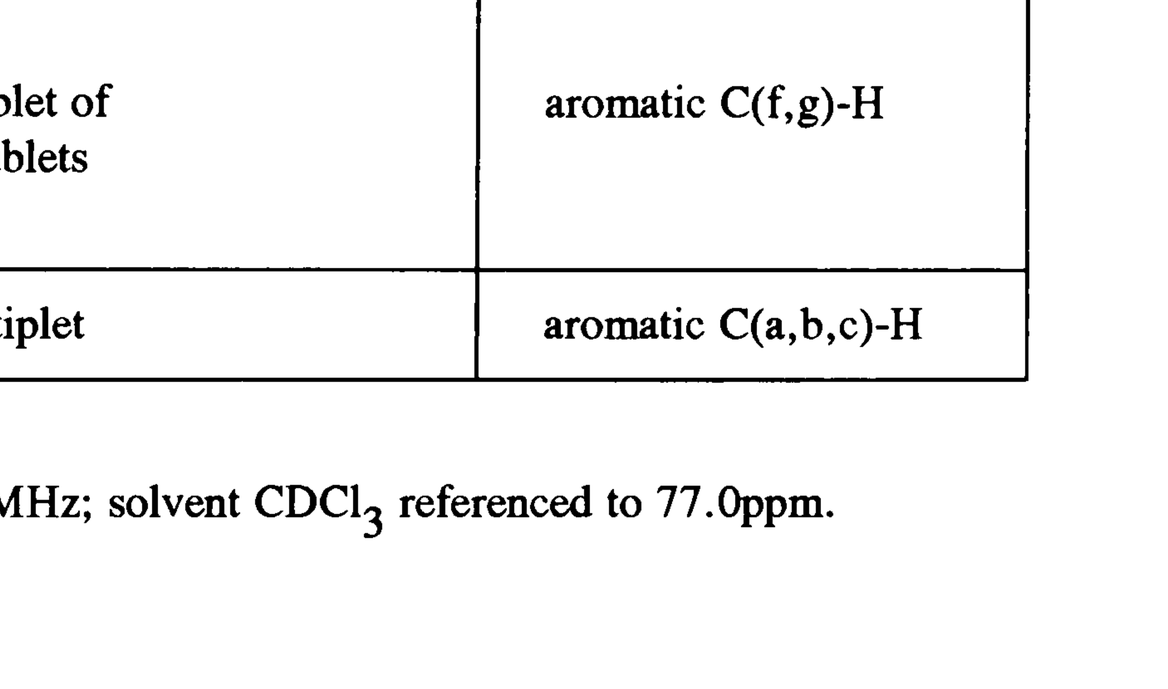
Mass spectrum (E.I.) A highest mass peak was observed at m/e 296 corresponding to the species $^{12}C_{12}{}^{1}H_9{}^{127}I{}^{16}O$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

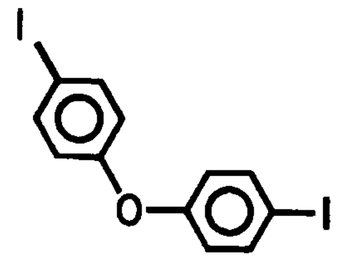
δ_{ppm}	intensity	type of peak	position of proton
7.64 7.60 6.80 6.76	4	doublet of doublets	aromatic C(f,g)-H
7.40-6.99	5	multiplet	aromatic C(a,b,c)-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
157.43	e
156.52	d
138.62	g
129.86	b
123.76	a
120.81	c
119.13	f
85.84	h



4,4′-diiododiphenyl ether



Melting point = 137-138°C (lit[27]. 139°C)

Analysis Found: C,33.8; H,1.8. $C_{12}H_8I_2$ requires C,34.1; H,1.9.

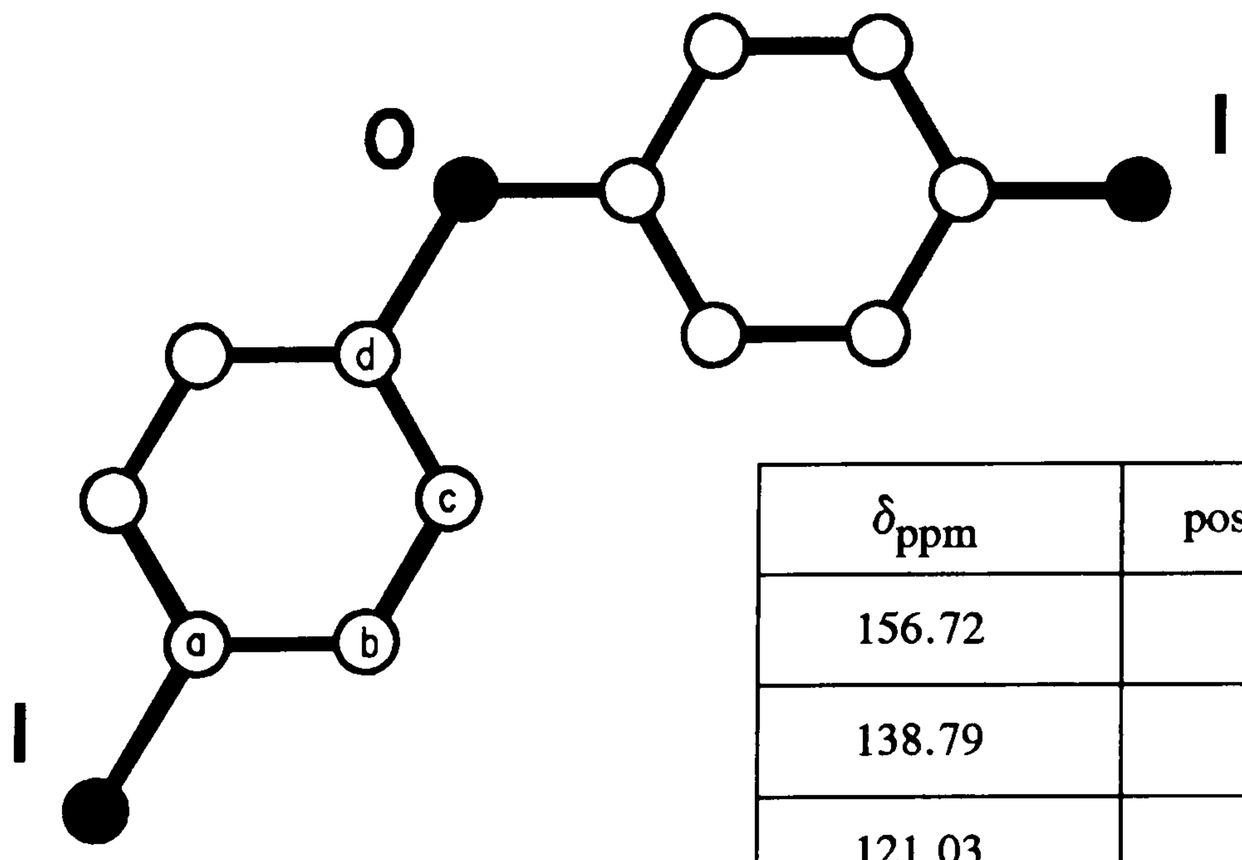
Infrared (KBr disc; cm^{-1}) 3108(w), 3091(w), 3068(w), 3048(w), 1898(w), 1592(w), 1578(m), 1565(w), 1482(s), 1468(m), 1440(w), 1432(w), 1401(w), 1398(w), 1305(w), 1299(w), 1281(m), 1269(m), 1261(m), 1252(s), 1247(s), 1239(m), 1198(w), 1172(m), 1110(w), 1098(w), 1075(w), 1062(w), 1043(w), 1023(w), 1008(m), 871(w), 836(w), 829(m), 818(s), 782(w), 752(w), 749(w), 691(w), 648(w), 637(w), 610(w), 603(w), 497(w), 491(w), 482(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 422 corresponding to the species $^{12}C_{12}{}^{1}H_8{}^{127}I_2{}^{16}O$. A peak at m/e 168 was also observed from $^{12}C_{12}{}^{1}H_8{}^{16}O$ fragment.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

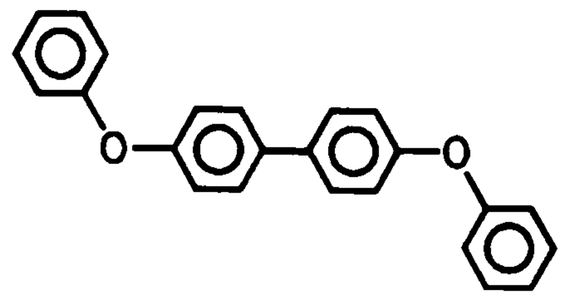
δ_{ppm}	intensity	type of peak	position of proton
7.65 7.61 6.78 6.74	8	doublet of doublets	aromatic C(b,c)-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.



δ_{ppm}	position of carbon
156.72	d
138.79	c
121.03	b
86.58	a

4,4′-diphenoxybiphenyl

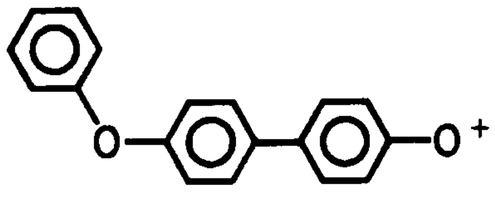


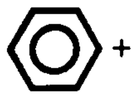
Melting point = 149-150°C (lit[31]. = 151-152°C)

Analysis Found: C,84.9; H,5.2. $C_{24}H_{18}O_2$ requires C,85.2; H,5.3.

Infrared (KBr disc; cm^{-1}) 3056(w), 3037(w), 2955(w), 2922(w), 2851(w), 2595(w), 2574(w), 2034(w), 1939(w), 1904(w), 1892(w), 1861(w), 1727(w), 1658(w), 1603(w), 1589(m), 1572(w), 1493(s), 1454(w), 1427(w), 1421(w), 1398(w), 1332(w), 1305(w), 1292(w), 1270(s), 1258(s), 1197(w), 1169(w), 1167(w), 1152(w), 1136(w), 1120(w), 1073(w), 1024(w), 1002(w), 983(w), 964(w), 900(w), 873(w), 832(s), 782(m), 748(m), 712(w), 693(m).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 338 corresponding to the species $^{12}C_{24}{}^{1}H_{18}{}^{16}O_2$. Two other peaks were also observed at m/e 261 and 77 assigned respectively to:





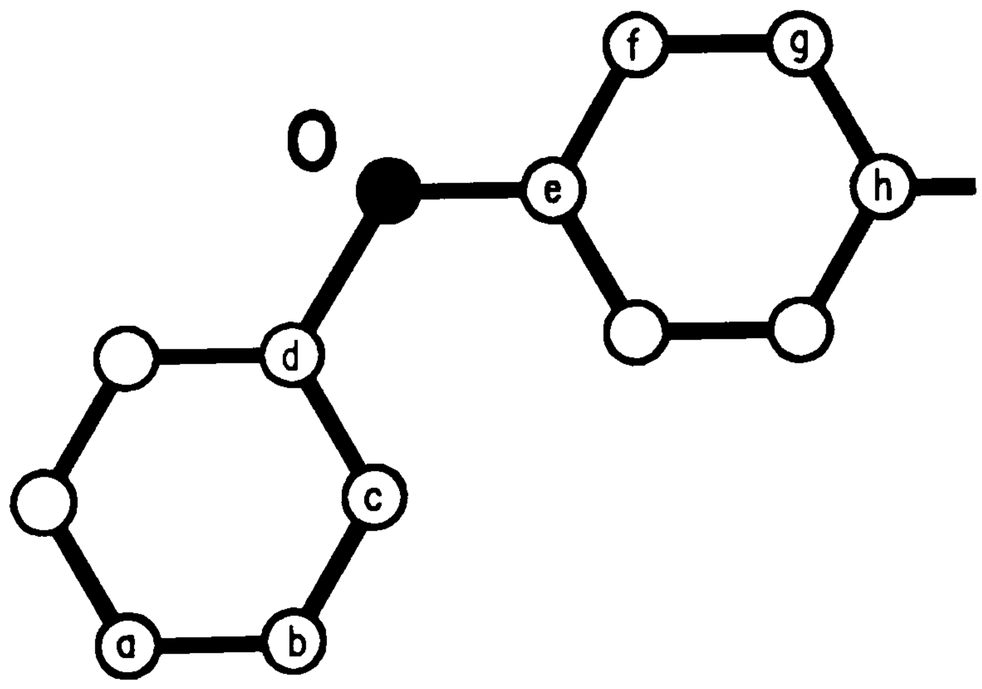
31. Takahashi H. Ohe K. Uemura S. Sugita N. *J. Organometal. Chem.* 1988 **350** 227-233

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

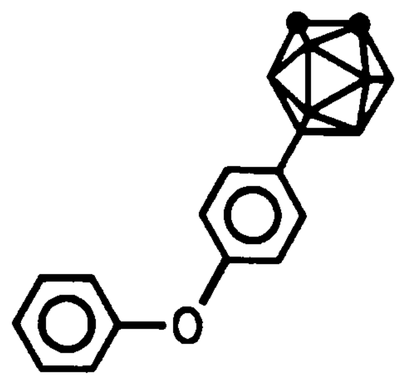
δ_{ppm}	intensity	type of peak	position of proton
7.46 7.42 7.00 6.96	8	doublet of doublets	aromatic C(f,g)-H
7.66-6.77	10	multiplet	aromatic C(a,b,c)-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
157.18	d
156.65	e
135.65	h
129.76	b
128.14	g
123.32	a
119.07	f
118.87	c

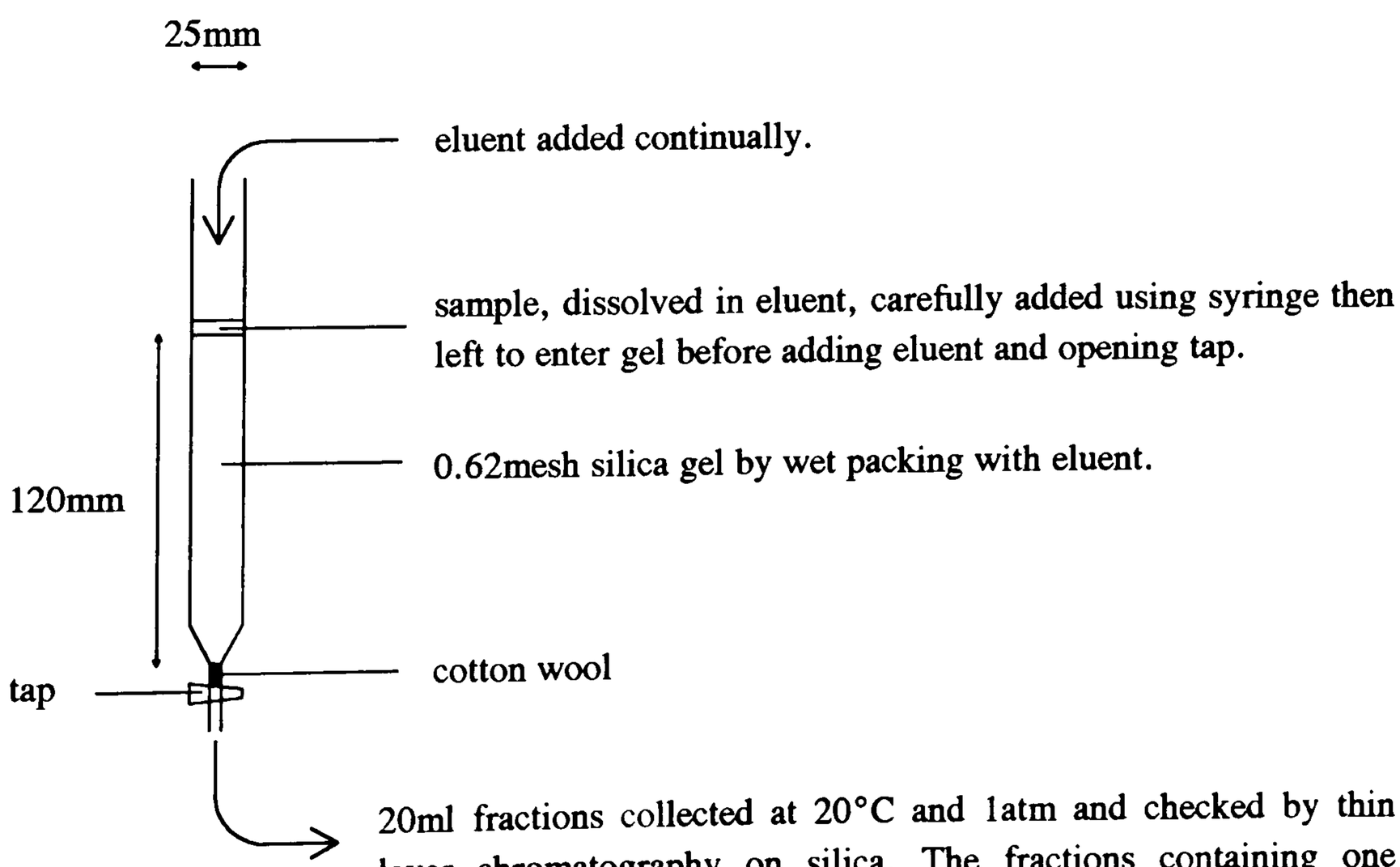


9-(4-phenoxyphenyl)-1,2-dicarba-*closo*-dodecaborane



11.84g (0.04 moles) of 4-iododiphenyl ether in 25ml of dry diethyl ether was added dropwise under a dry nitrogen atmosphere to 1.5g (0.06 moles) of magnesium filings and an iodine crystal in 15ml dry diethyl ether at 0°C. After reaction, the excess filings were filtered off under nitrogen and the filtrate was added to a stirred solution of 2.70g (0.01 moles) 9-iodo-*ortho*-carborane and 0.04g (0.0568 mmoles) bis(triphenylphosphino)palladium dichloride in 30ml dry diethyl ether. The solution was refluxed under nitrogen for 36 hours. After cooling, the black mixture was decomposed with 100ml of distilled water and the organic layer was washed with two 20ml portions each of hydrochloric acid and distilled water. The organic layer was dried over anhydrous magnesium sulphate, filtered and the ether removed by rotary evaporator. From the residue, by two runs of column chromatography with 1.1g of sample and hexane as eluent, 1.88g (60.3%) of 9-(4-phenoxyphenyl)-*ortho*-carborane was obtained.

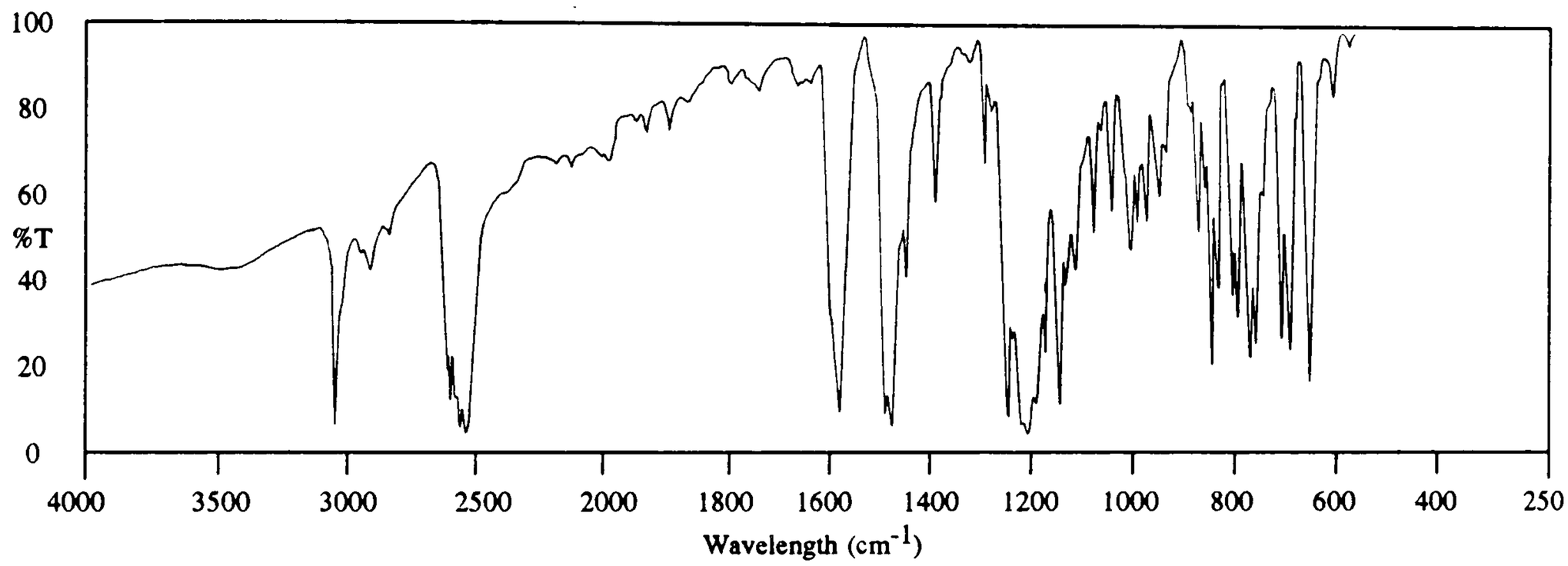
Apparatus used for column chromatography



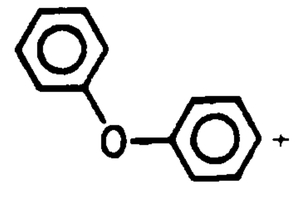
Melting point = 177-178°C

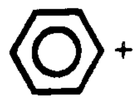
Analysis Found: C,54.9; H,6.7. $C_{14}H_{20}B_{10}O$ requires C,53.9; H,6.4.

Infrared (KBr disc; cm^{-1}) 3055(s), 2958(w), 2923(w), 2853(w), 2640(s), 2628(s), 2611(s), 2596(s), 2571(s), 1586(s), 1500(s), 1488(s), 1455(m), 1398(w), 1307(w), 1292(w), 1269(s), 1256(m), 1240(s), 1232(s), 1213(s), 1196(m), 1169(s), 1157(m), 1138(m), 1103(w), 1088(w), 1068(w), 1036(m), 1021(w), 1004(w), 979(w), 967(w), 922(w), 918(w), 906(w), 892(w), 882(s), 868(m), 842(m), 831(m), 810(s), 798(m), 791(w), 749(m), 732(s), 718(w), 696(s), 643(w), 610(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 314 corresponding to the species $^{12}C_{14}{}^{1}H_{20}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 308 and 314. Peaks present at m/e 169 and 77 were probably, respectively, from:





^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.46 7.42 6.80 6.77	4	doublet of doublets	aromatic C(f,g)-H
7.31-7.17 7.07-6.90	5	multiplet	aromatic C(a,b,c)-H
3.54	1	broad singlet	carboranyl C(j)-H
3.44	1	broad singlet	carboranyl C(i)-H
4.0-0.9	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

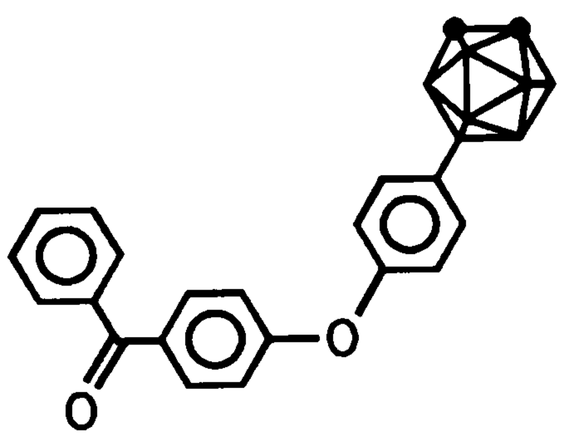
δ_{ppm}	intensity	position of boron
7.29	1	9
-2.49	1	12
-8.96	2	8,10
-14.47	4	4,5,7,11
-15.52	2	3,6

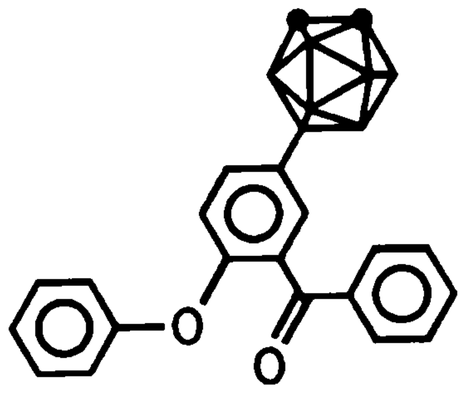
^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
157.28	d
156.87	e
133.75	g
129.63	b
123.02	a
118.94	f
117.81	c
53.14	i
48.67	j

Attempted formation of 9-(4′-benzoyl-4-phenoxyphenyl)-1,2-dicarba-*closo*-dodecarborane

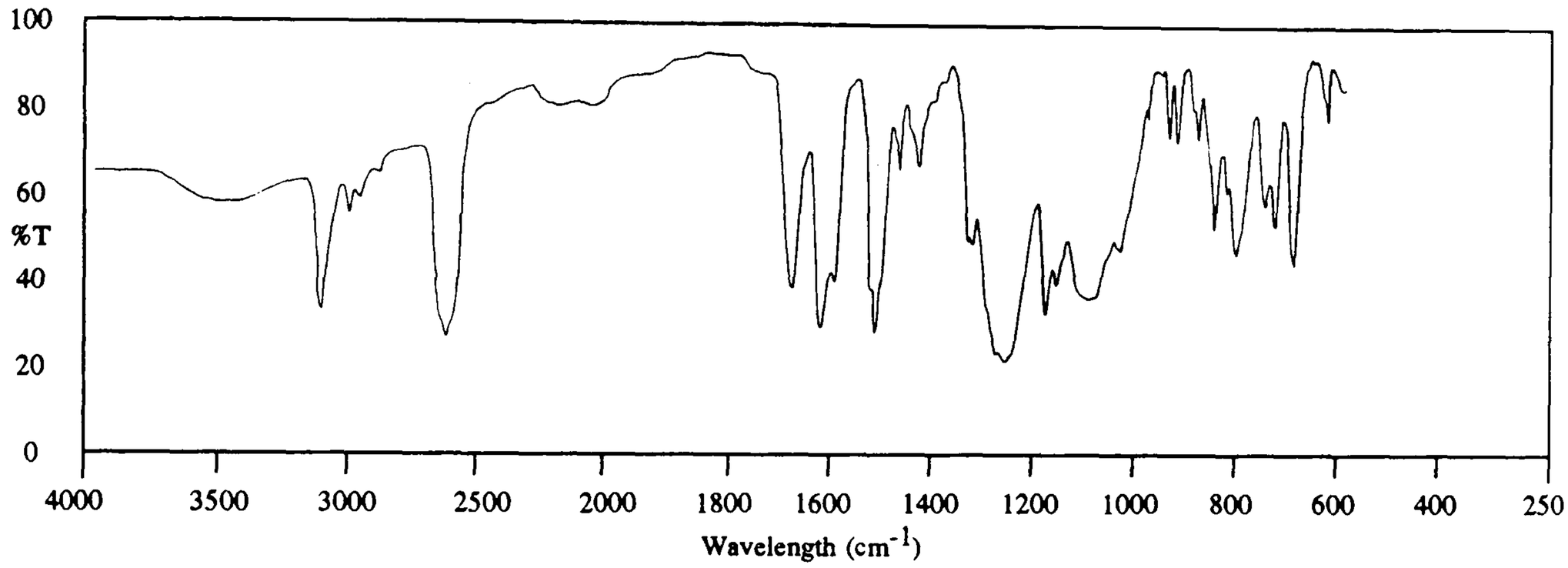
8ml TFSA was added to a powdered mixture of 0.312g (1 mmole) 9-(4-phenoxyphenyl)-*ortho*-carborane and 0.122g (1 mmole) benzoic acid under nitrogen with stirring. The red solution was left standing for 24 hours and then poured into 30ml distilled water to give an off-white precipitate which was filtered off, washed with 5% sodium hydroxide solution and distilled water and dried *in vacuo*. The 0.26g solid contained two compounds according to thin layer chromatography using hexane as eluent which could not be separated by column chromatography on silica with hexane. From characterization data, the compounds are probably 9-(4′-benzoyl-4-phenoxyphenyl)-*ortho*-carborane and 9-(3-benzoyl-4-phenoxyphenyl)-*ortho*-carborane.





Analysis Found: C,62.1; H,6.0. $C_{21}H_{24}B_{10}O_2$ requires C,60.6; H,5.8.

Infrared (KBr disc; cm^{-1}) 3065(s), 3052(m), 2968(w), 2932(w), 2861(w), 2632(s), 2605(s), 2583(s), 1653(s), 1599(s), 1573(m), 1504(s), 1494(s), 1459(w), 1451(w), 1419(w), 1414(w), 1401(w), 1386(w), 1368(w), 1321(m), 1311(m), 1280(s), 1265(s), 1252(s), 1249(s), 1239(s), 1172(s), 1152(m), 1143(m), 1105(s), 1078(s), 1058(m), 1041(m), 1033(m), 1021(m), 1008(w), 995(w), 985(w), 961(w), 945(w), 929(w), 897(w), 888(w), 855(m), 832(m), 812(m), 806(m), 758(m), 738(m), 701(m), 674(w), 664(w), 642(w), 609(w).

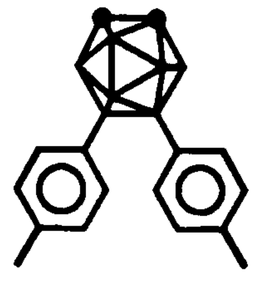


Mass spectrum (E.I.) A highest mass peak was observed at m/e 418 corresponding to the species $^{12}C_{21}{}^{1}H_{24}{}^{11}B_{10}{}^{16}O_2$, accompanied by the usual carborane isotope distribution pattern between m/e 412 and 418.

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm. A poor spectrum was obtained so peak assignments were not attempted.

Observed peaks; 139.17, 137.98, 137.30, 136.82, 133.99, 132.40, 132.03, 131.47, 130.47, 129.73, 128.96, 128.17, 125.24, 124.11, 123.35, 120.44, 119.30, 118.87, 117.12, 116.77, 53.28(br), 50.63(br), 49.27(br). The broad peaks are probably carboranyl carbons which indicate two carborane derivatives present.

9,12-bis(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

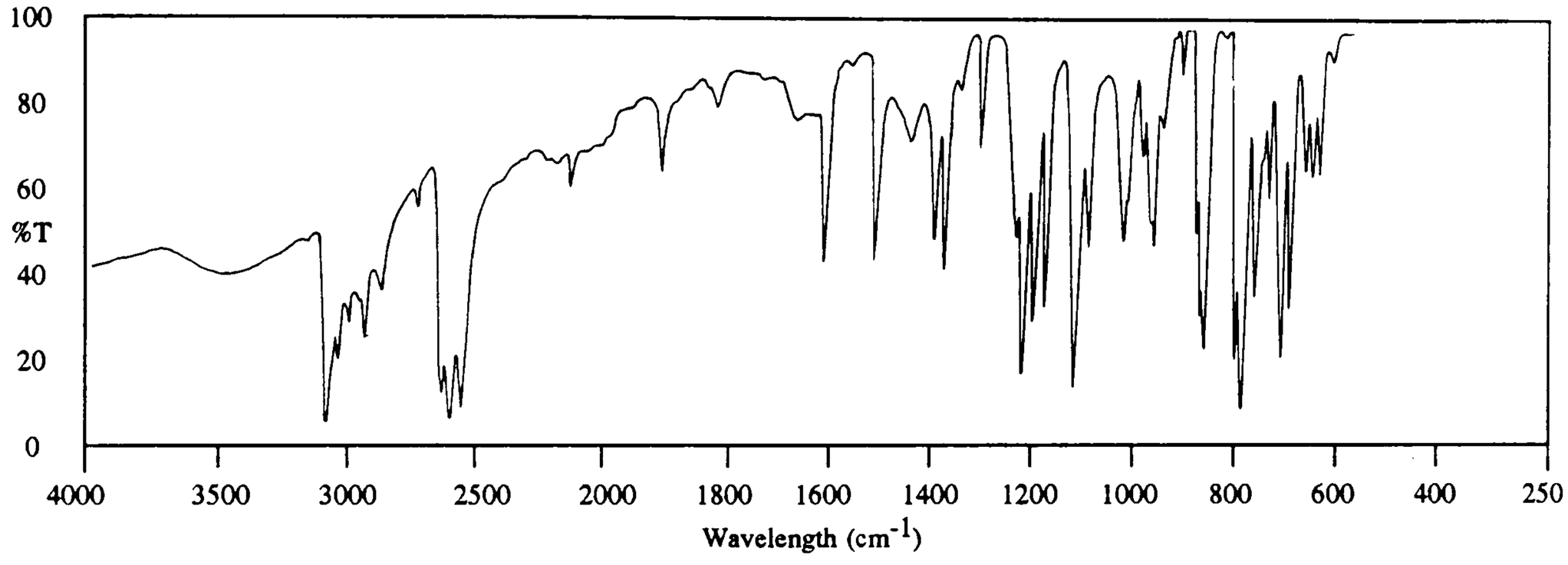


A stirred solution of 17.44g (0.08 moles) 4-iodotoluene in 40ml dry diethyl ether was added dropwise under a dry nitrogen atmosphere to 3g (0.12 moles) of magnesium turnings in 20ml anhydrous diethyl ether at 0°C. After reaction, the excess magnesium was filtered off under nitrogen and the filtrate was added to a solution of 3.96g (0.01 moles) 9,12-diiodo-*ortho*-carborane and 0.04g (0.0568 mmoles) of catalyst, Bis(triphenylphosphino)palladium dichloride, in 20ml anhydrous diethyl ether. The solution was refluxed under nitrogen for 24 hours. After cooling, the black mixture was decomposed with 100ml of distilled water and the organic layer was washed with two 30ml portions each of hydrochloric acid and distilled water. A precipitate formed in the organic layer which was filtered off, washed with fresh diethyl ether and recrystallized from hot toluene to give 1.04g (32.1%) of 9,12-bis(4-methylphenyl)-*ortho*-carborane.

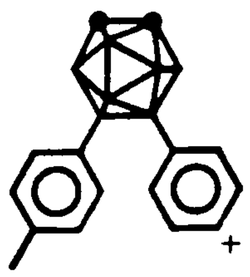
Melting point = 277.5-278°C

Analysis Found: C,59.1; H,7.3. $C_{16}H_{24}B_{10}$ requires C,59.3; H,7.4.

Infrared (KBr disc; cm^{-1}) 3138(w), 3056(s), 3018(m), 2978(w), 2941(w), 2917(w), 2857(w), 2726(w), 2629(s), 2594(s), 2556(s), 2155(w), 1912(w), 1808(w), 1658(w), 1602(m), 1553(w), 1507(m), 1439(w), 1394(m), 1376(m), 1348(w), 1308(w), 1308(w), 1239(m), 1227(s), 1209(m), 1186(m), 1131(s), 1105(m), 1079(w), 1037(m), 1028(w), 1001(w), 984(m), 979(m), 962(w), 925(w), 899(m), 890(m), 881(m), 842(w), 822(m), 810(s), 784(m), 760(w), 735(m), 720(m), 691(w), 678(w), 662(w), 638(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 326 corresponding to the species $^{12}C_{16}{}^{1}H_{24}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 320 and 326. A group of peaks between m/e 305 and 311 were also shown assigned to:



^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

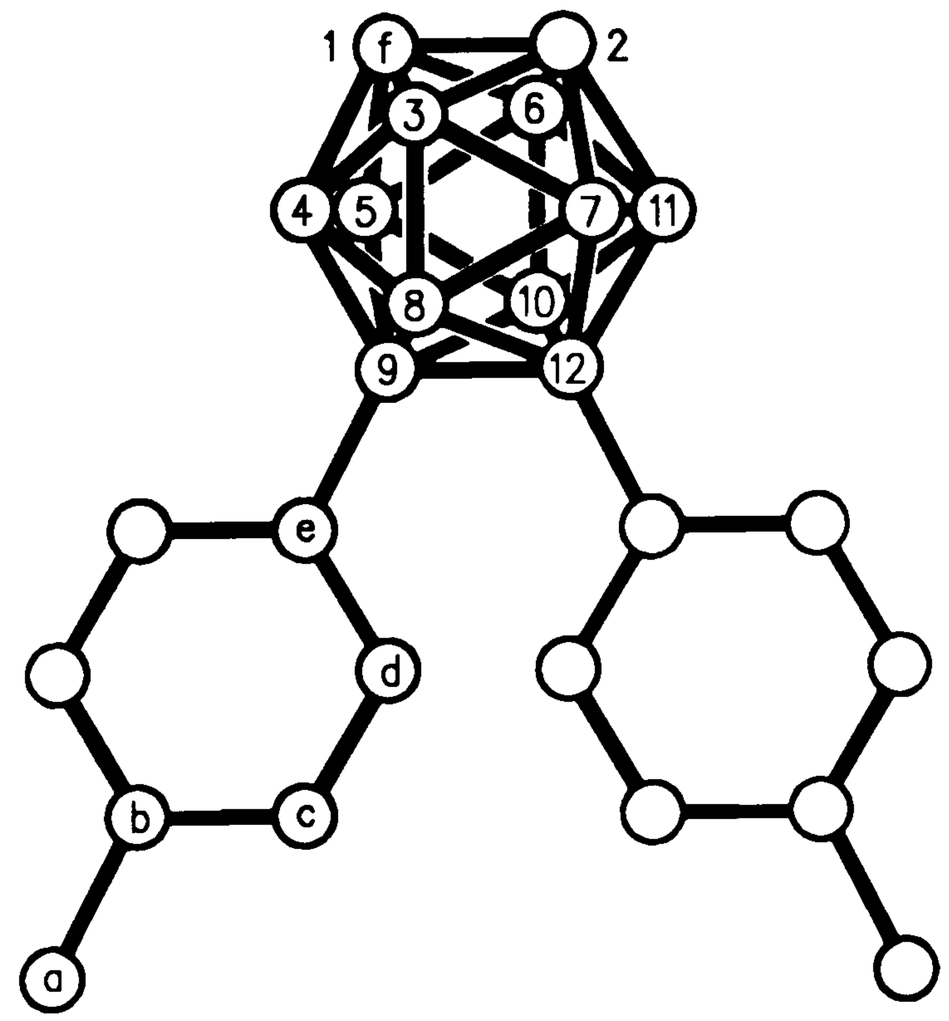
δ_{ppm}	intensity	type of peak	position of proton
6.97 6.94 6.76 6.73	4	doublet of doublets	aromatic C(c,d)-H
4.48	2	broad singlet	carboranyl C(f)-H
2.04	3	singlet	methyl C(a)-H
4.0-0.8	8	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

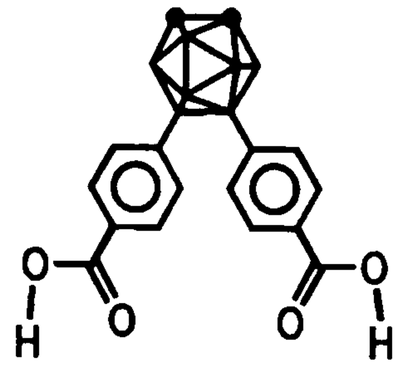
δ_{ppm}	intensity	position of boron
8.24	2	9,12
-9.13	2	8,10
-14.06	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$ referenced to 28.0ppm.

δ_{ppm}	position of carbon
135.06	b
131.86	d
126.86	c
49.63	f
19.30	a



9,12-bis(4-carboxyphenyl)-1,2-dicarba-*closo*-dodecaborane

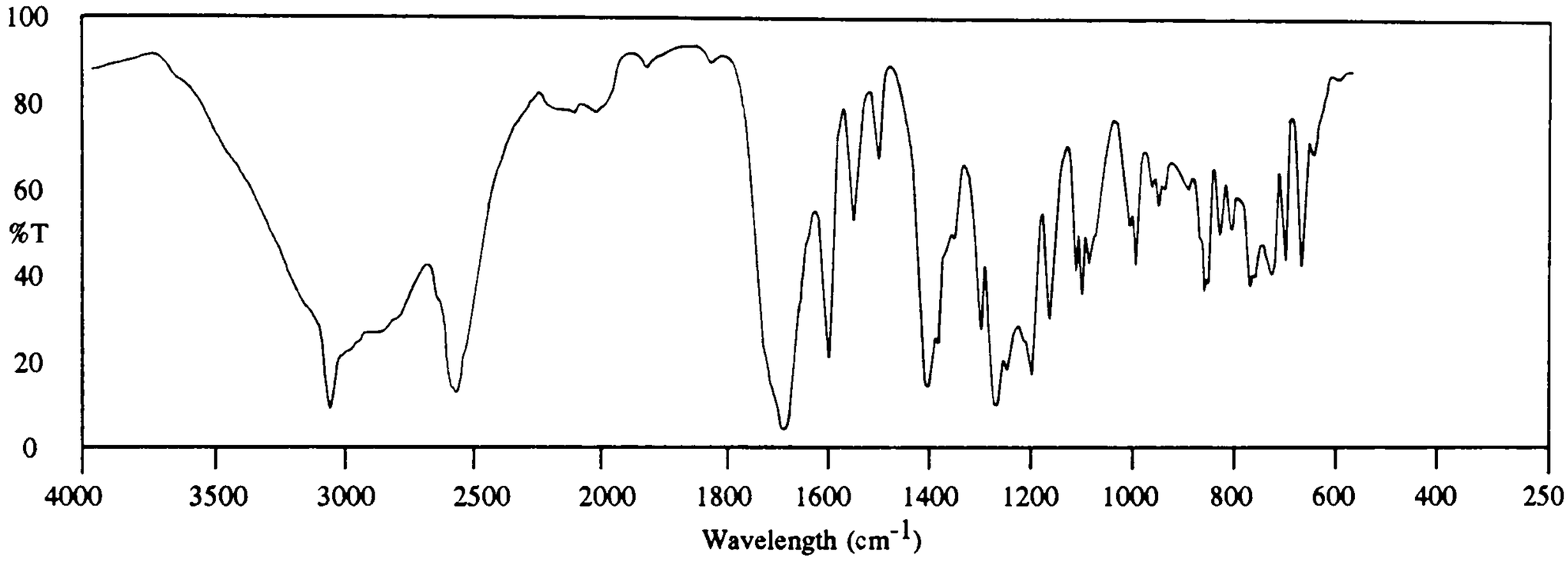


3g (30 mmoles) of chromium (IV) trioxide was gradually added to a stirred solution of 0.648g (2 mmoles) 9,12-bis(4-methylphenyl)-*ortho*-carborane, 7.5ml acetic anhydride and 1.5ml concentrated sulphuric acid in 30ml glacial acetic acid at 20°C. After two hours the green mixture was poured into 250ml of cold distilled water. The organic products were extracted from the green aqueous solution into three 30ml portions of diethyl ether. The extracts were combined, dried over anhydrous magnesium sulphate, filtered and the solvent was removed by rotary evaporator to leave a pale green solid. The solid was dissolved in boiling sodium hydrogen carbonate solution, some insoluble solid was filtered off, then the solution was acidified with dilute hydrochloric acid to give an off-white precipitate. The precipitate was filtered off, washed thoroughly with distilled water and dried over phosphorus pentoxide to give 0.49g (63.8%) of 9,12-bis(4-carboxyphenyl)-*ortho*-carborane as white powder.

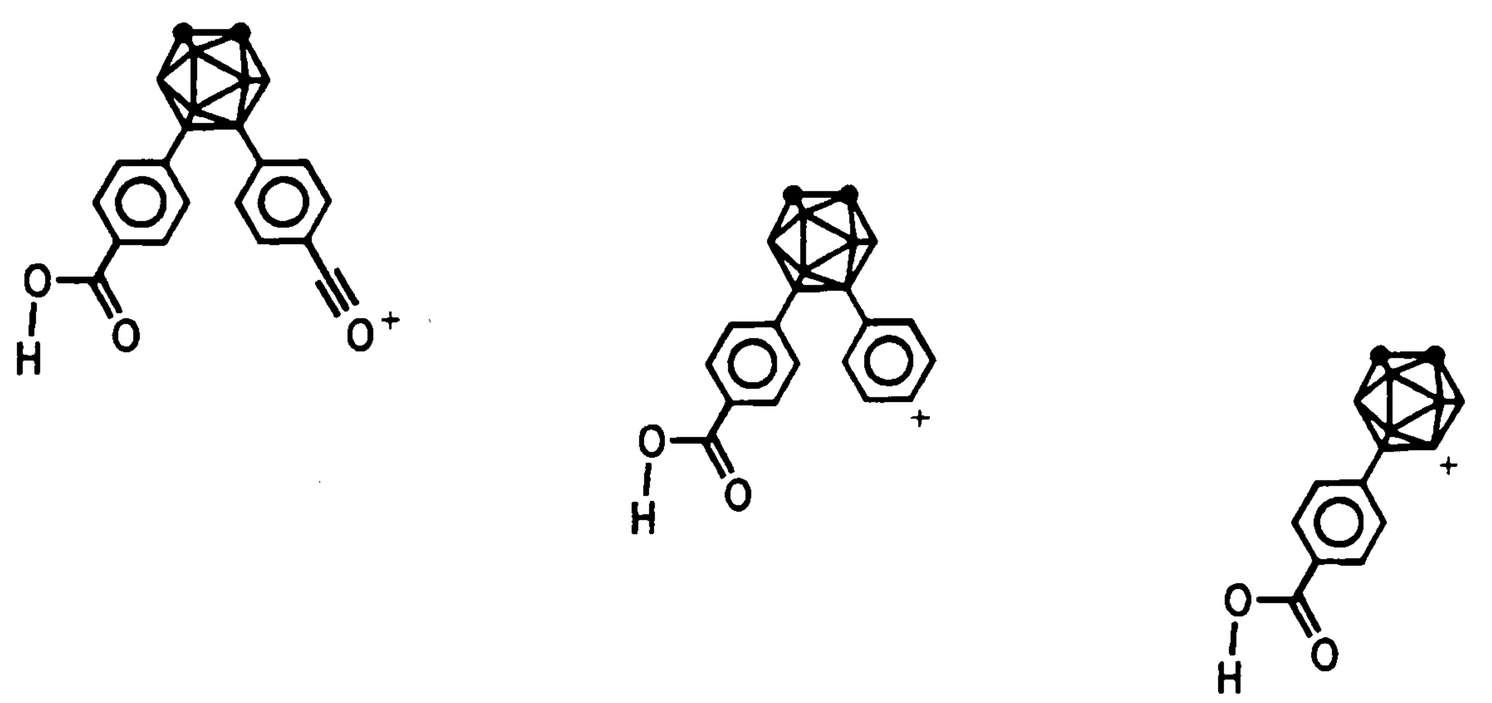
Melting point = 312-313°C

Analysis Found: C,49.7; H,5.4. $C_{16}H_{20}B_{10}O_4$ requires C,50.0; H,5.2.

Infrared (KBr disc; cm^{-1}) 3650-2330(m,br), 3061(s), 2655(m), 2617(s), 2596(s), 2561(s), 1939(w), 1820(w), 1687(s), 1598(s), 1551(w), 1503(w), 1414(s), 1396(s), 1381(m), 1363(w), 1314(m), 1288(s), 1267(s), 1232(m), 1219(s), 1186(m), 1135(m), 1123(m), 1110(m), 1101(m), 1032(w), 1021(m), 991(w), 978(w), 968(w), 921(w), 899(w), 890(m), 883(m), 860(w), 838(w), 802(m), 794(m), 772(m), 763(m), 734(m), 704(m), 681(w).



Mass spectrum (C.I.-) A highest mass peak was observed at m/e 386 corresponding to the species $^{12}C_{16}{}^{1}H_{20}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 380 and 386. Three groups of peaks were also observed at m/e 364-370, 342-346 and 261-267 assigned respectively to:



^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.65 7.62 7.21 7.18	8	doublet of doublets	aromatic C(c,d)-H
4.68	2	broad singlet	carboranyl C(f)-H
4.0-0.8	8	broad multiplet	carboranyl B-H

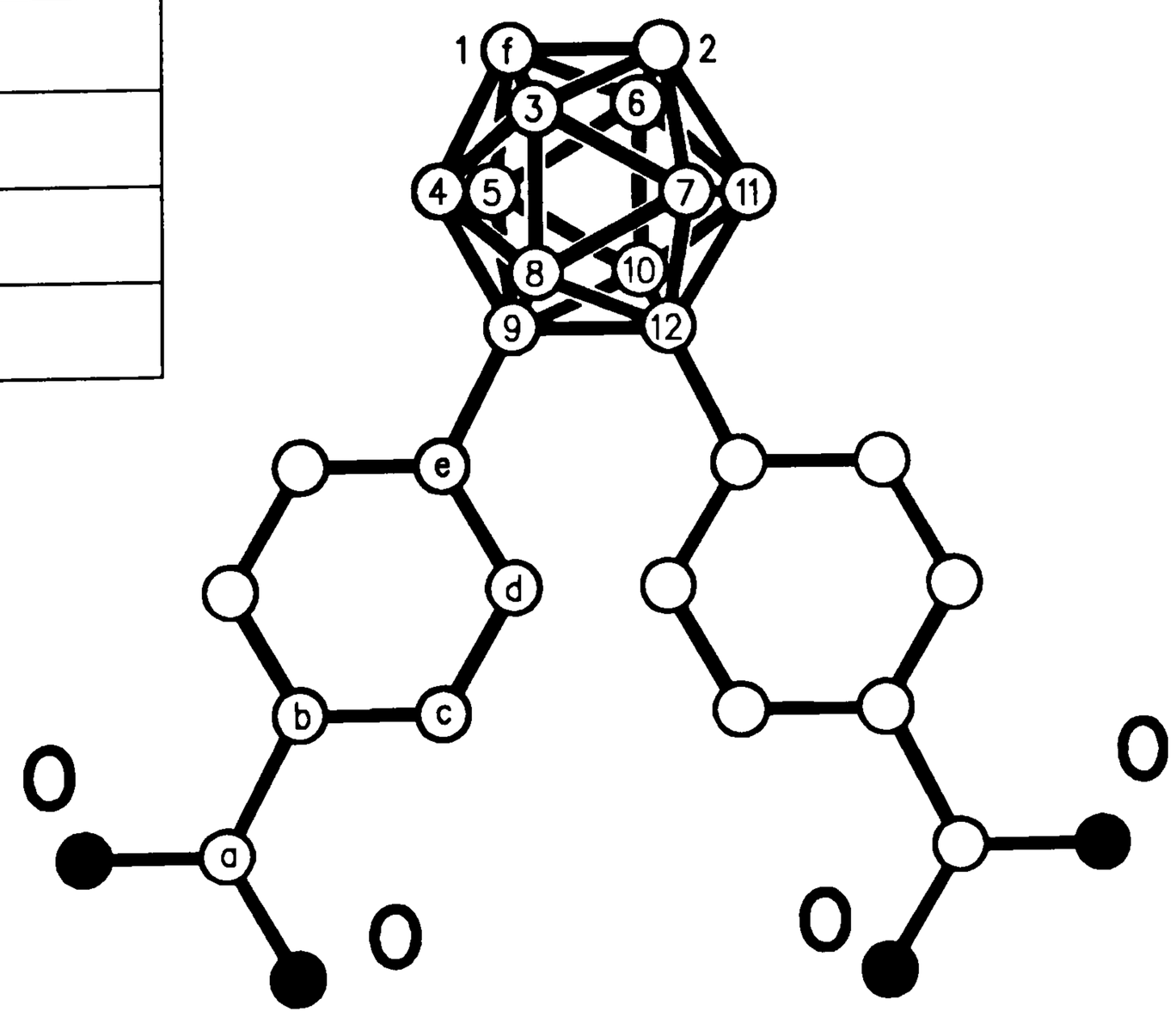
The carboxylic proton peak is not seen between -1 and 20ppm.

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

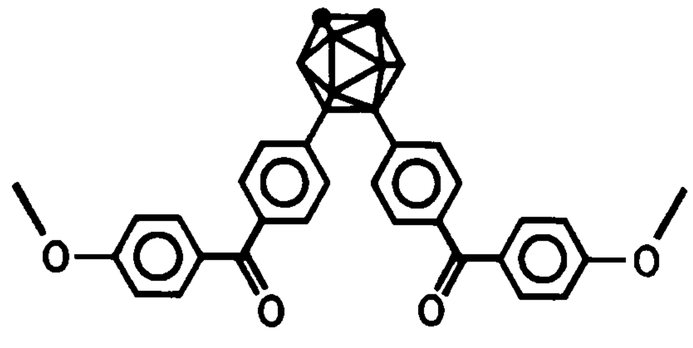
δ_{ppm}	intensity	position of boron
7.63	2	9,12
-8.71	2	8,10
-12.61	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$ referenced to 28.0ppm.

δ_{ppm}	position of carbon
165.92	a
131.81	b
128.15	d
127.26	c
50.77	f



9,12-bis(4′-methoxy-4-benzoylphenyl)-1,2-dicarba-*closo*-dodecaborane

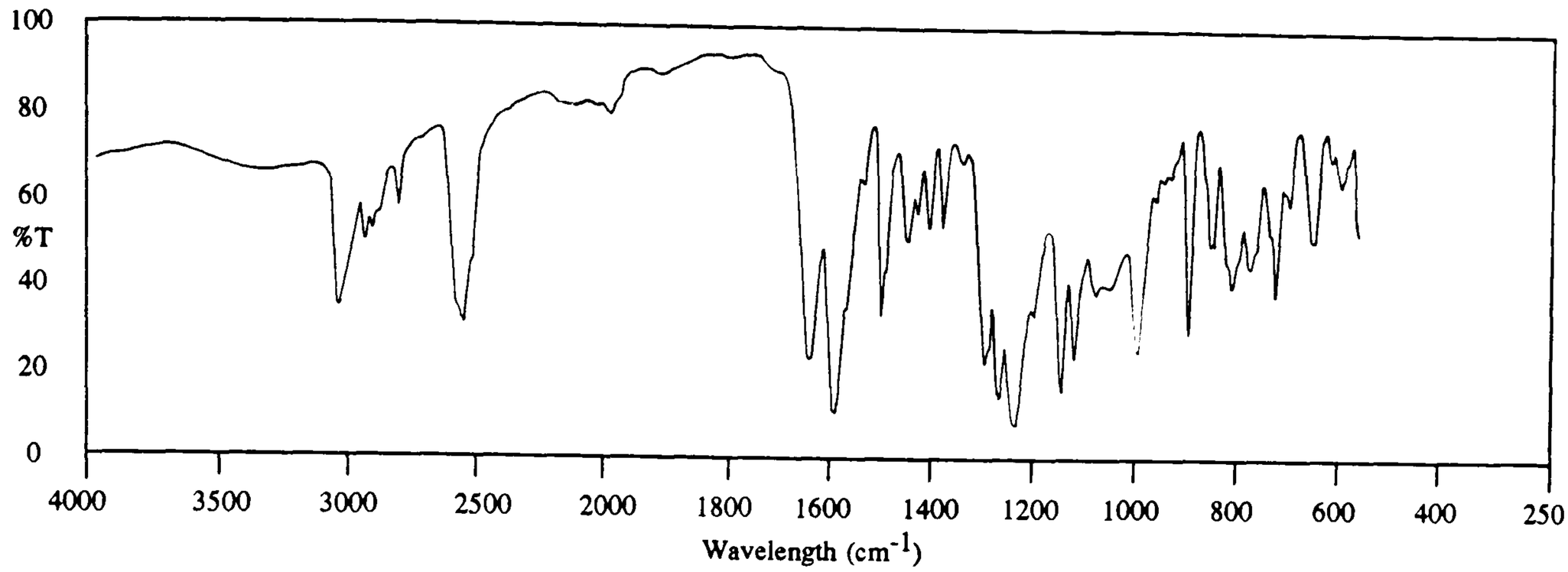


0.384g (1 mmoles) 9,12-bis(4-carboxyphenyl)-*ortho*-carborane and 0.24g (2.2 mmoles) anisole were dissolved in 4ml TFSA and left to stand for 24 hours under nitrogen. The dark red solution was poured into water giving a white precipitate which was extracted with two portions of diethyl ether. The diethyl ether extracts were washed with 10% sodium hydroxide, water and dried over anhydrous magnesium sulphate. The ether was removed by rotary evaporator leaving a solid which was recrystallized from hexane to give 0.41g (72.7%) of 9,12-bis(4′-methoxy-4-benzoylphenyl)-*ortho*-carborane.

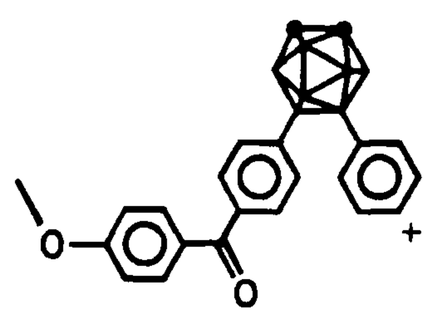
Melting point = 209-210°C

Analysis Found: C,59.5; H,5.6. $C_{30}H_{32}B_{10}O_4$ requires C,59.6; H,5.7.

Infrared (KBr disc; cm^{-1}) 3061(m), 3011(w), 2963(w), 2937(w), 2918(w), 2840(w), 2618(m), 2599(m), 2577(m), 2053(w), 1647(s), 1601(s), 1581(m), 1548(w), 1512(m), 1507(m), 1462(w), 1443(w), 1422(w), 1396(w), 1359(w), 1318(s), 1309(s), 1289(s), 1260(s), 1228(m), 1176(s), 1152(s), 1114(m), 1089(m), 1083(m), 1032(s), 997(w), 982(w), 970(w), 958(w), 933(m), 899(w), 892(w), 858(w), 849(m), 813(w), 805(w), 772(w), 765(m), 746(w), 740(w), 695(w), 691(w), 659(w), 642(w), 636(w), 628(w), 602(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 566 corresponding to the species $^{12}C_{30}{}^{1}H_{32}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 560 and 566. Peaks shown between m/e 425 and 431 correspond with:



^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

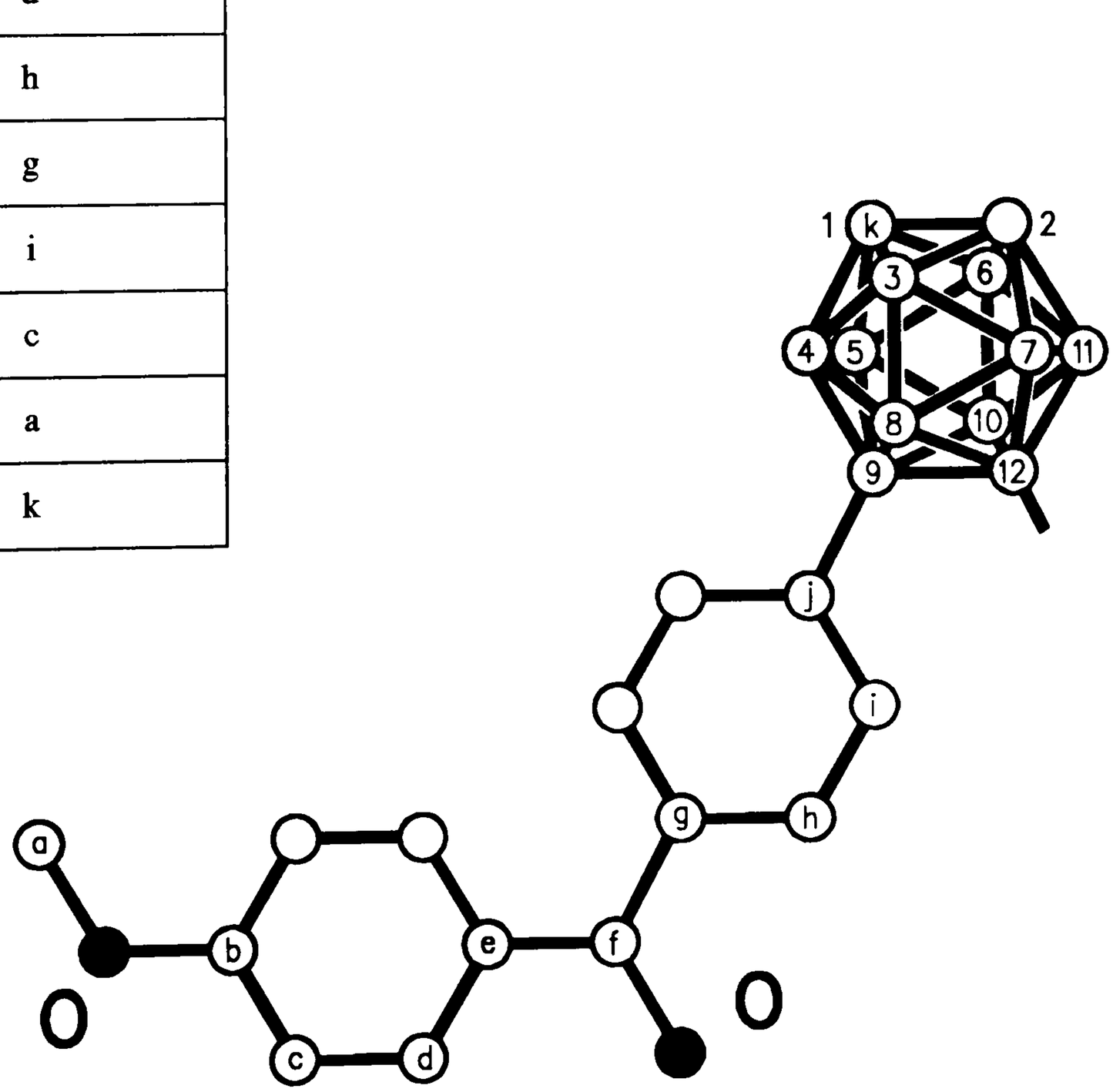
δ_{ppm}	intensity	type of peak	position of proton
7.68 7.64 6.84 6.80	4	doublet of doublets	aromatic C(c,d)-H
7.42 7.39 7.23 7.20	4	doublet of doublets	aromatic C(h,i)-H
3.75	6	singlet	methyl C(a)-H
3.66	2	broad singlet	carboranyl C(k)-H
4.1-1.0	8	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

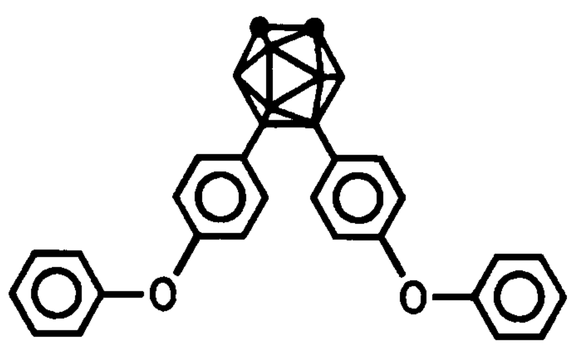
δ_{ppm}	intensity	position of boron
7.99	2	9,12
-8.55	2	8,10
-13.01	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
195.93	f
163.05	b
136.76	e
132.68	d
132.52	h
130.28	g
128.65	i
113.46	c
55.48	a
50.13	k

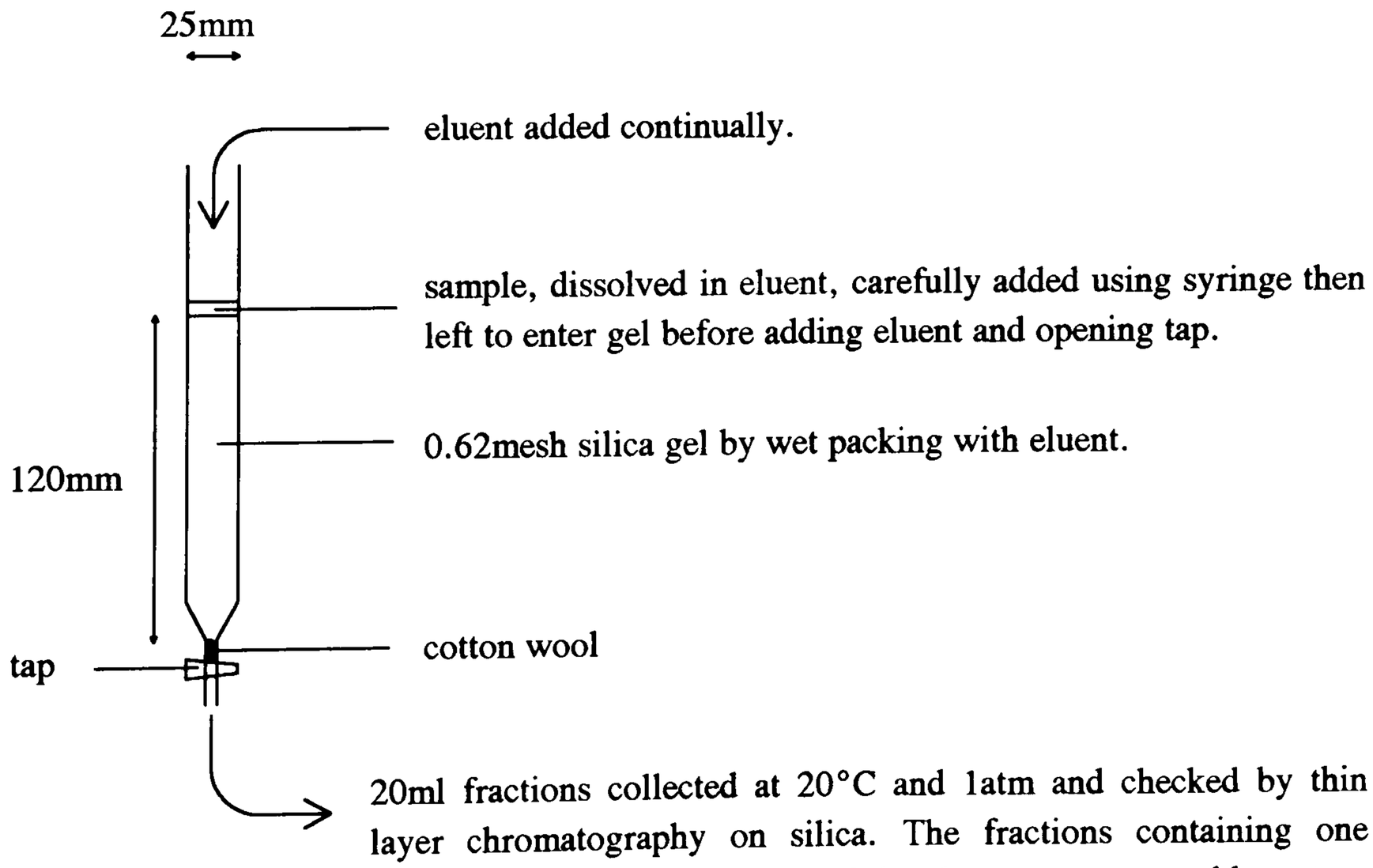


9,12-bis(4-phenoxyphenyl)-1,2-dicarba-*closo*-dodecaborane



A solution of 11.84g (0.04 moles) of 4-iododiphenyl ether in 25ml of dry diethyl ether was added dropwise to 1.5g (0.06 moles) of magnesium filings in 15ml anhydrous diethyl ether at 0°C under nitrogen. After reaction, the excess filings were filtered off under nitrogen and the filtrate was added to a solution of 1.98g (5 mmoles) 9,12-diiodo-*ortho*-carborane and 0.04g (0.0568 mmoles) bis(triphenylphosphino)palladium dichloride in 20ml diethyl ether. The solution was refluxed under nitrogen for 48 hours. The black mixture was cooled and decomposed with 100ml of distilled water. The organic layer was separated, washed with two 20ml portions each of hydrochloric acid and distilled water, dried over anhydrous magnesium sulphate and filtered. The ether was removed *in vacuo* and from the residue, by column chromatography with 0.9g of residue and hexane as eluent, 0.7g (29.2%) of 9,12-bis(4-phenoxyphenyl)-*ortho*-carborane was obtained.

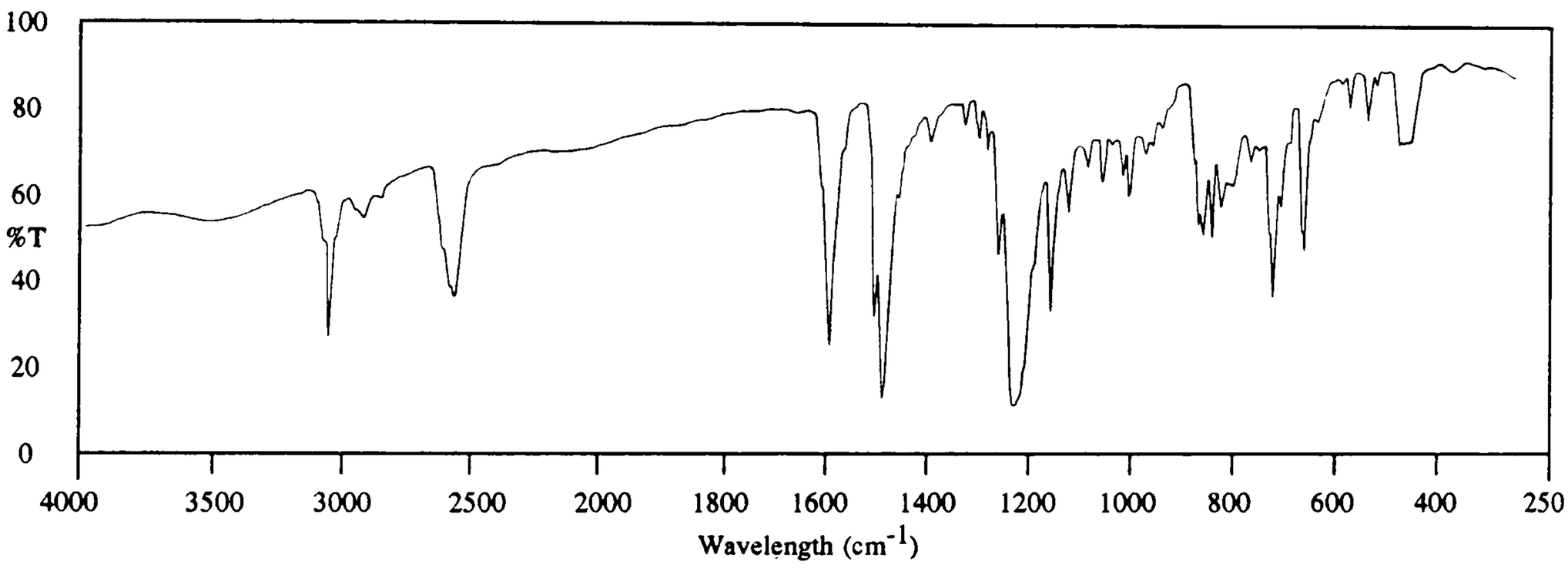
Apparatus used for column chromatography



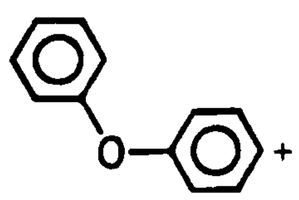
Melting point = 125-126°C

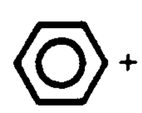
Analysis Found: C,65.5; H,5.9. $C_{26}H_{28}B_{10}O_2$ requires C,65.0; H,5.8.

Infrared (KBr disc; cm^{-1}) 3070(w), 3053(s), 3031(w), 2960(w), 2926(w), 2859(w), 2631(s), 2602(s), 2584(s), 1604(w), 1588(s), 1564(w), 1505(m), 1490(s), 1458(m), 1398(w), 1336(w), 1309(w), 1292(w), 1270(m), 1242(s), 1234(s), 1209(m), 1172(m), 1138(m), 1101(w), 1074(w), 1057(w), 1036(w), 1024(w), 1022(w), 990(w), 978(w), 961(w), 945(w), 899(w), 891(m), 882(m), 867(m), 847(m), 835(w), 828(w), 821(w), 792(w), 776(w), 769(w), 755(m), 748(m), 733(w), 719(w), 692(m), 689(m), 678(w), 666(w), 635(w), 607(w), 570(w), 553(w), 509(w), 498(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 482 corresponding to the species $^{12}C_{26}{}^{1}H_{28}{}^{11}B_{10}{}^{16}O_2$, accompanied by the usual carborane isotope distribution pattern between m/e 476 and 482. Two peaks were also observed at m/e 169 and 77 assigned respectively to:





^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

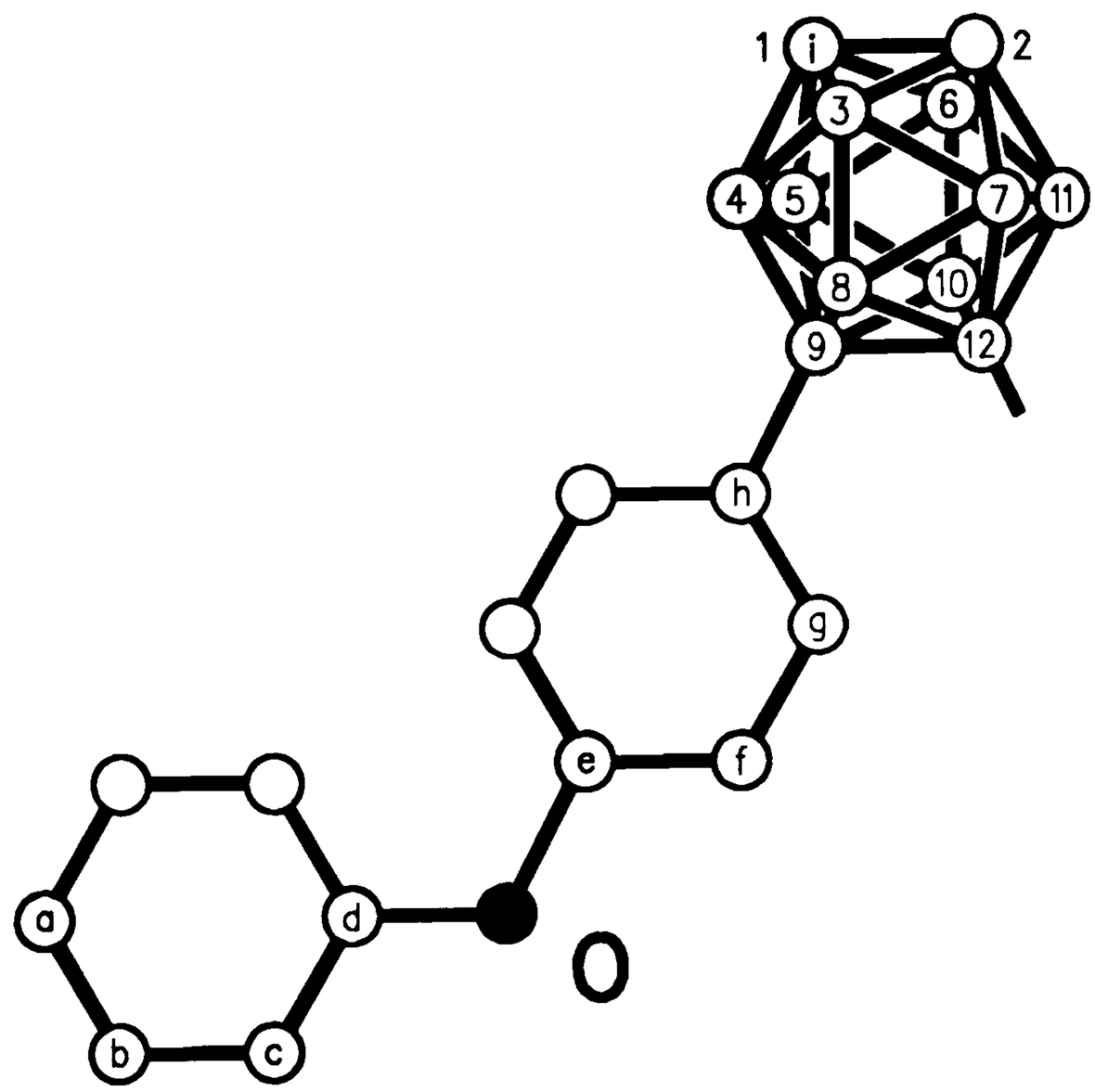
δ_{ppm}	intensity	type of peak	position of proton
7.29-7.19 7.05-7.00 6.80-6.71	10	multiplet	aromatic C(a,b,c)-H
7.16 7.13 6.94 6.91	8	doublet of doublets	aromatic C(f,g)-H
3.53	2	broad singlet	carboranyl C(i)-H
4.0-1.2	8	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

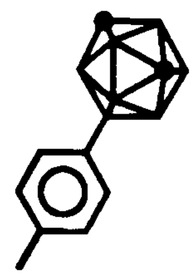
δ_{ppm}	intensity	position of boron
8.15	2	9,12
-8.95	2	8,10
-14.02	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
157.21	d
156.61	e
134.35	g
129.66	b
123.12	a
119.06	f
117.88	c
49.14	i

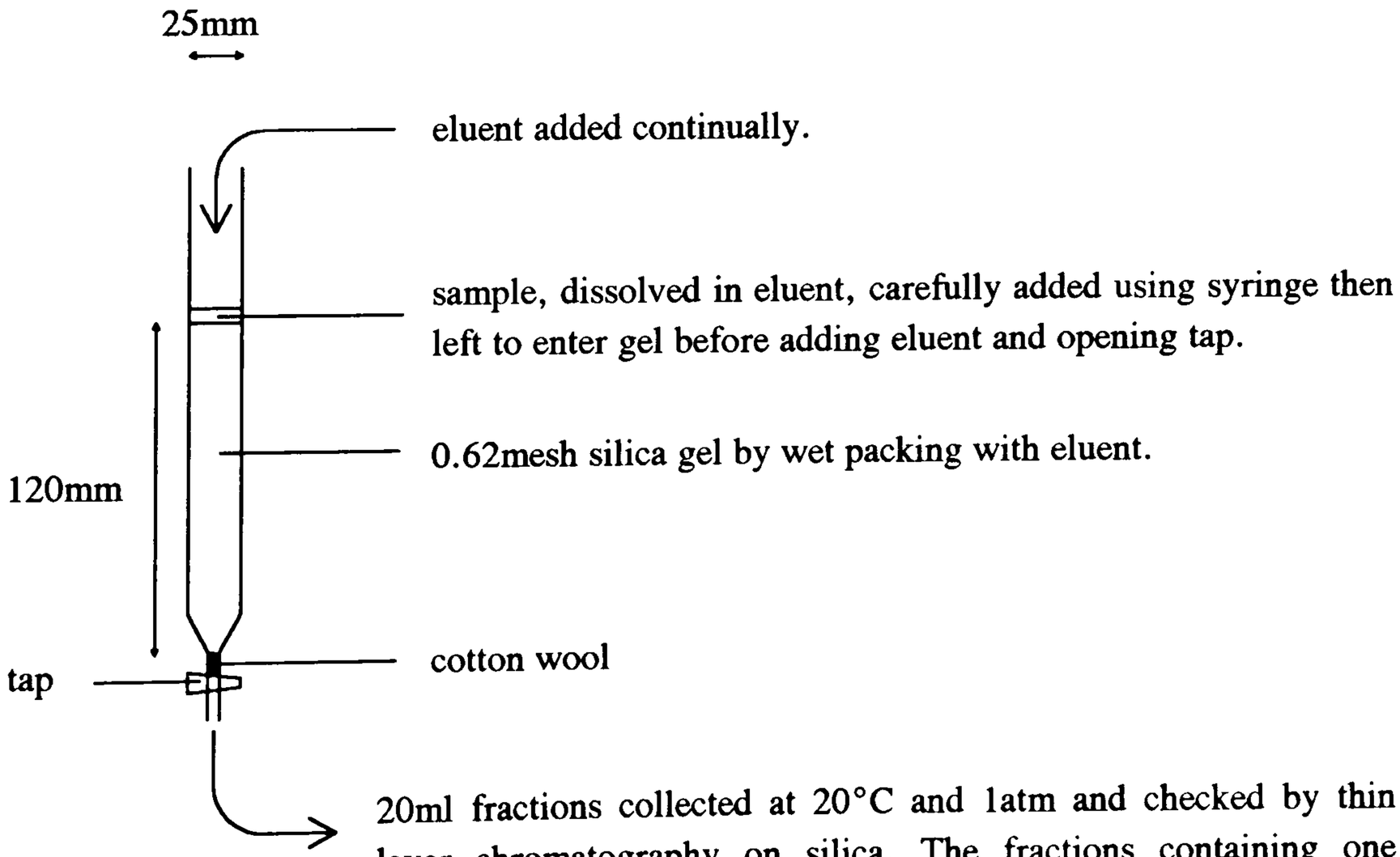


9-(4-methylphenyl)-1,7-dicarba-*closo*-dodecaborane



A solution of 8.72g (0.04 moles) 4-iodotoluene in 20ml diethyl ether was added dropwise under a dry nitrogen atmosphere to 1.5g (0.06 moles) magnesium filings in 15ml diethyl ether at 0°C. A crystal of iodine was required to initiate the reaction. After reaction, the excess filings were filtered off under nitrogen and the filtrate was added to a solution of 2.70g (0.01 moles) 9-iodo-1,7-*meta*-carborane and 0.04g (0.0568 mmoles) bis(triphenylphosphino)palladium dichloride, in 30ml diethyl ether. The solution was refluxed under nitrogen for 24 hours. After cooling, the black mixture was decomposed with 100ml of distilled water and the organic layer was washed with two 30ml portions each of hydrochloric acid and distilled water. The organic layer was dried over anhydrous magnesium sulphate, filtered and the ether removed by rotary evaporator. The residue was found by thin layer chromatography on silica using hexane as eluent to contain two main products which were separated by two runs of column chromatography with 1.6g of sample and hexane as eluent to give 2.4g of pure 4,4′-dimethylbiphenyl and 0.8g (34.2%) of 9-methylphenyl-*meta*-carborane.

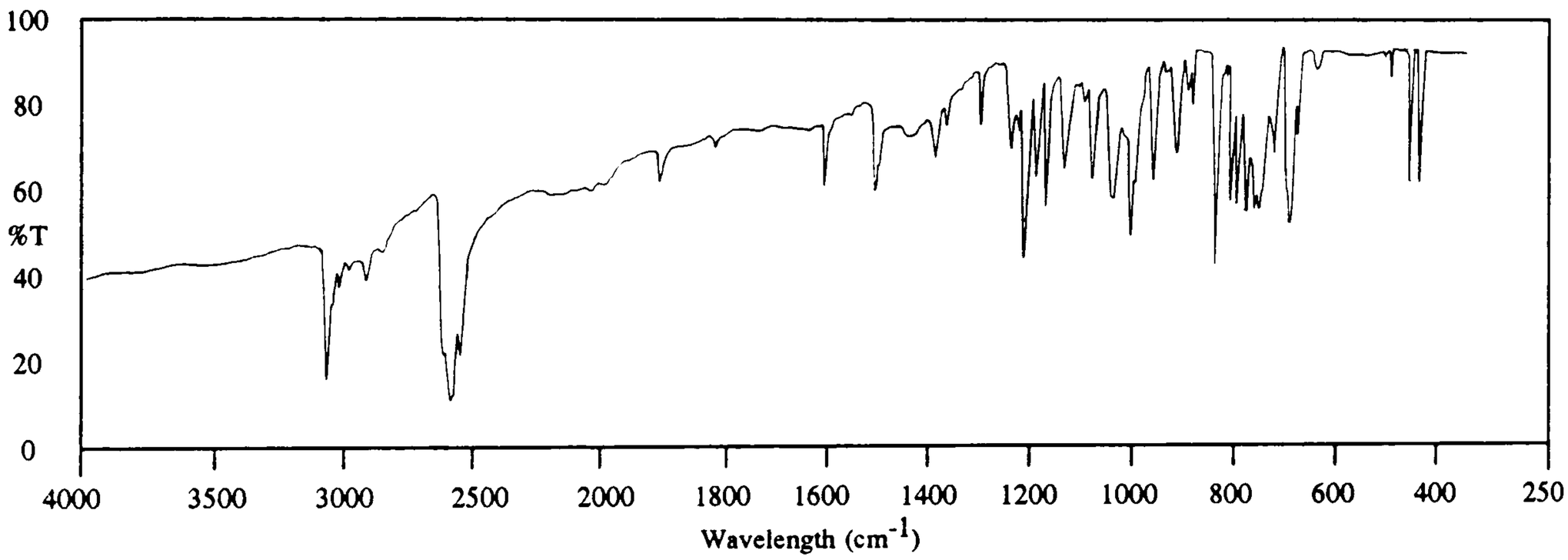
Apparatus used for column chromatography



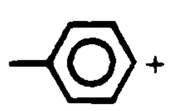
Melting point = 72-73°C (lit[18]. 73-74°C)

Analysis Found: C,46.3; H,7.6. $C_9H_{18}B_{10}$ requires C,46.2; H,7.7.

Infrared (KBr disc; cm^{-1}) 3132(w), 3065(s), 3048(w), 3023(w), 2988(w), 2982(w), 2925(w), 2872(w), 2634(s), 2604(s), 2598(s), 2573(s), 1918(w), 1915(w), 1813(w), 1610(m), 1558(w), 1511(m), 1505(m), 1450(w), 1437(w), 1398(w), 1379(w), 1354(w), 1314(w), 1282(w), 1258(w), 1243(w), 1232(s), 1210(m), 1192(m), 1157(m), 1130(w), 1121(w), 1105(m), 1069(m), 1064(m), 1041(w), 1031(s), 1024(m), 990(m), 968(w), 964(w), 947(m), 927(w), 918(w), 870(s), 861(w), 851(w), 840(m), 830(m), 812(m), 798(m), 789(m), 783(m), 760(m), 732(m), 730(m), 727(m), 715(w), 680(w), 676(w), 549(w), 537(w), 499(m), 481(m).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 236 corresponding to the species $^{12}C_9{}^{1}H_{18}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 230 and 236. A peak at m/e 91 was also present and assigned to $C_7H_7{}^{+}$, i.e.:

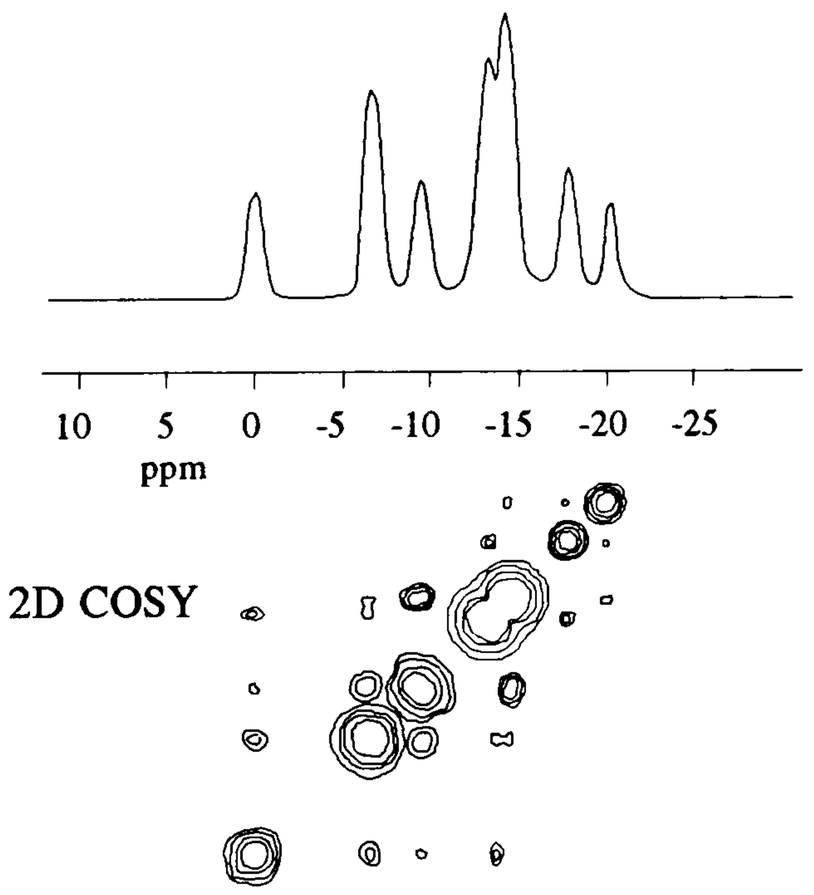


^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.46 7.43 7.15 7.12	4	doublet of doublets	aromatic C-H
3.00	2	broad singlet	carboranyl C-H
2.36	3	singlet	methyl C-H
3.9-1.0	9	broad multiplet	carboranyl B-H

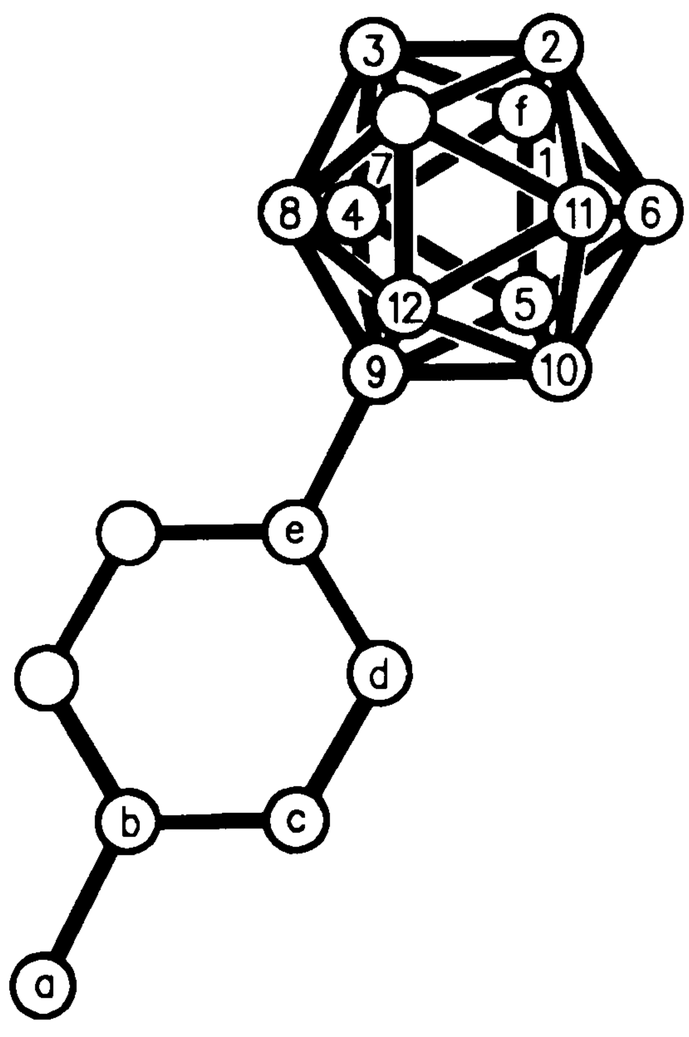
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
0.16	1	9
-6.79	2	5,12
-9.86	1	10
-13.35	2	4,8
-14.08	2	6,11
-17.74	1	3
-20.15	1	2



^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
137.02	b
133.08	d
128.36	c
54.12	f
21.14	a



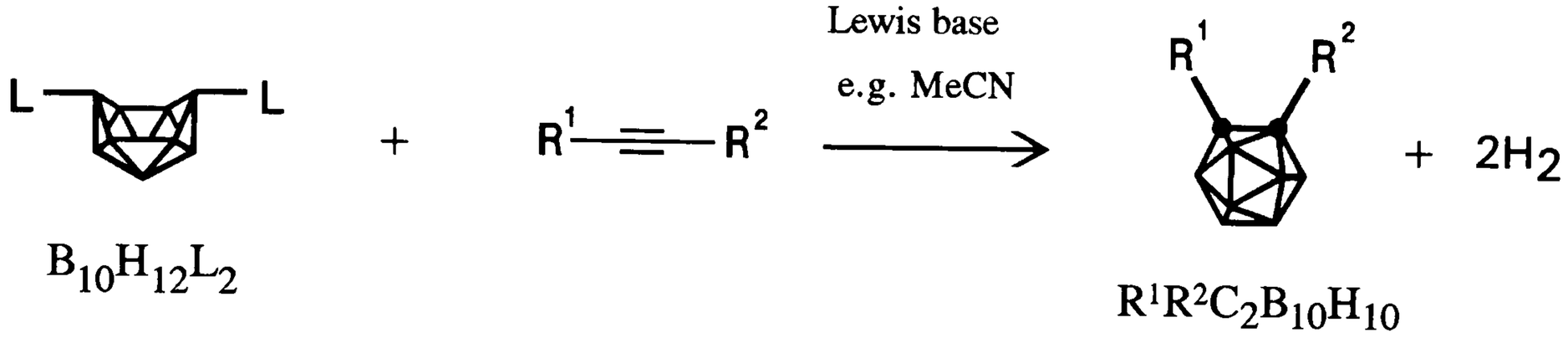
CHAPTER 7

CARBON-ARYL CARBORANES

The preparations and reactions of carbon-aryl carboranes are described in this chapter. It also includes the syntheses and model reactions of potential carbon-aryl carborane monomers for CPEK formation.

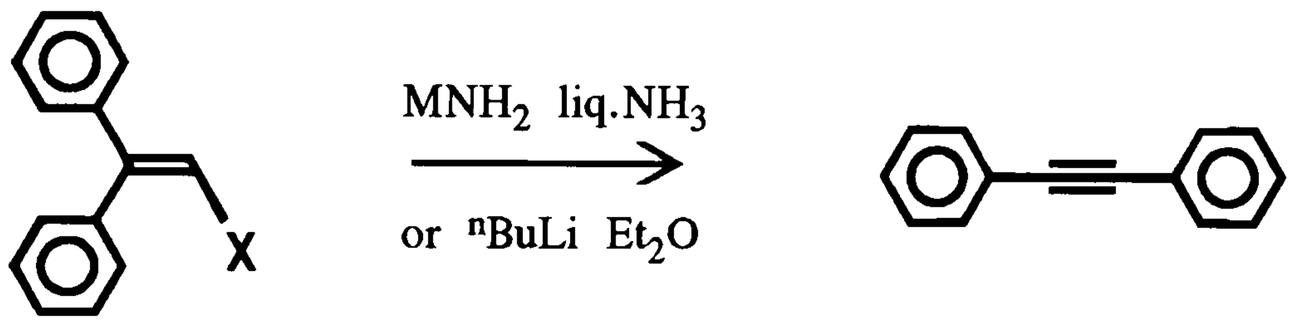
FORMATION OF CARBON-ARYL CARBORANES

1-aryl- and 1,2-diaryl-*ortho*-carboranes are usually produced by reacting suitable monoarylacetylenes and diarylacetylenes respectively with 6,9-bis(ligand)-decaborane[1,2,3].



R^1 = aryl, R^2 = H or aryl

Monoaryl- and diarylacetylenes can be obtained from elimination reactions of 2-halogeno-1,1-diarylethenes with alkali metal amides[4,5,6], *neo*-butyllithium[7], α-diketones with triethylphosphite[8], α-diketones with hydrazine followed by a silver salt[9] and 3-nitroso-2-oxazolidones with alkali[10].



X = Br or Cl, M = K or Na

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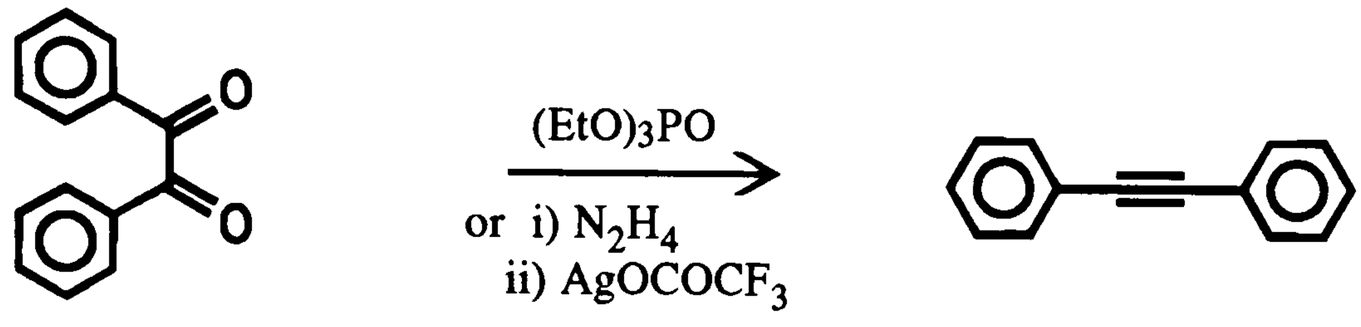

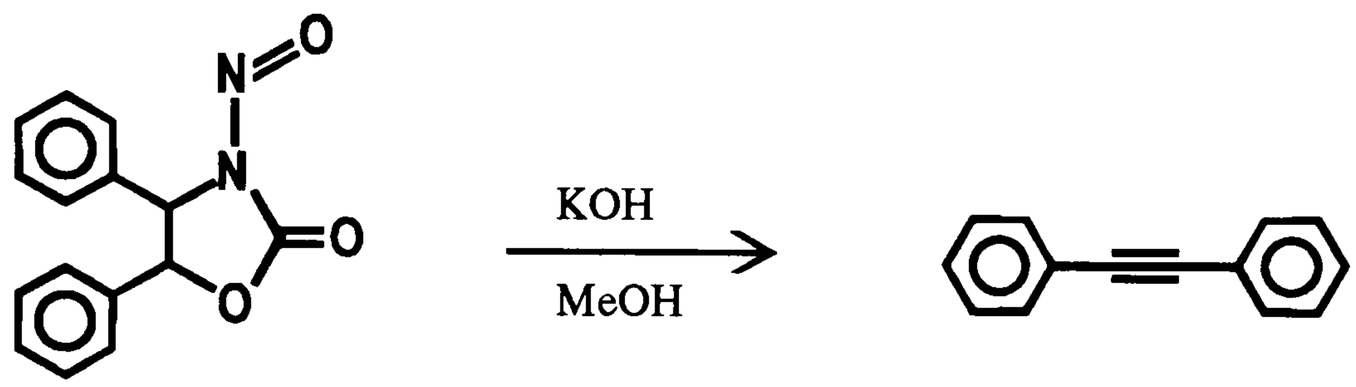

Coupling reactions of unsubstituted or monoarylsubstituted acetylenes and aryl iodides can also give monoaryl- and diarylacetylenes. The reactions use catalysts like copper powder[11], copper iodide[12,13,14,15,16,17,18], nickel and palladium complexes[13,15,16,17,18,19,20,21], bases like potassium carbonate[11,12,14,18], sodium methoxide[20], aqueous sodium hydroxide[15], triethylamine[16,17,21] and diethylamine[13,19] and solvents like triethylamine[16,21], diethylamine[13,17,19], benzene[15,17], chloroform[17], pyridine[14], dimethylformamide[11,17,18,20], acetone[17] and tetrahydrofuran[17]. Copper arylacetylides, formed by a monoarylsubstituted acetylene with copper iodide in

11. Shvartsberg M.S. Kotlyarevskii I.L. Kozhevnikova A.N. Andrievskii V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1970 1079-1082
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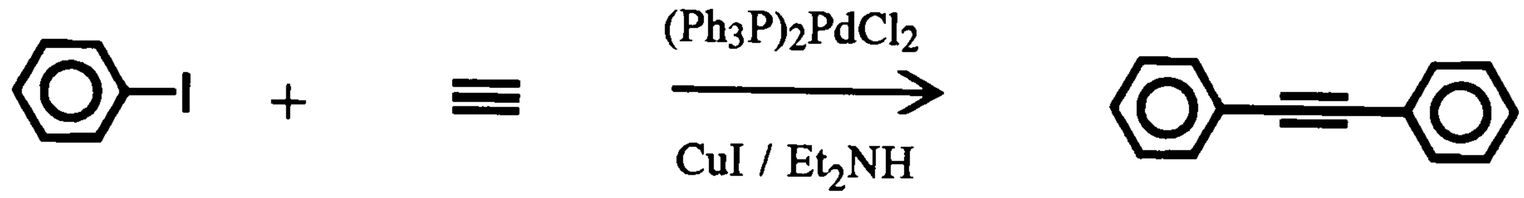
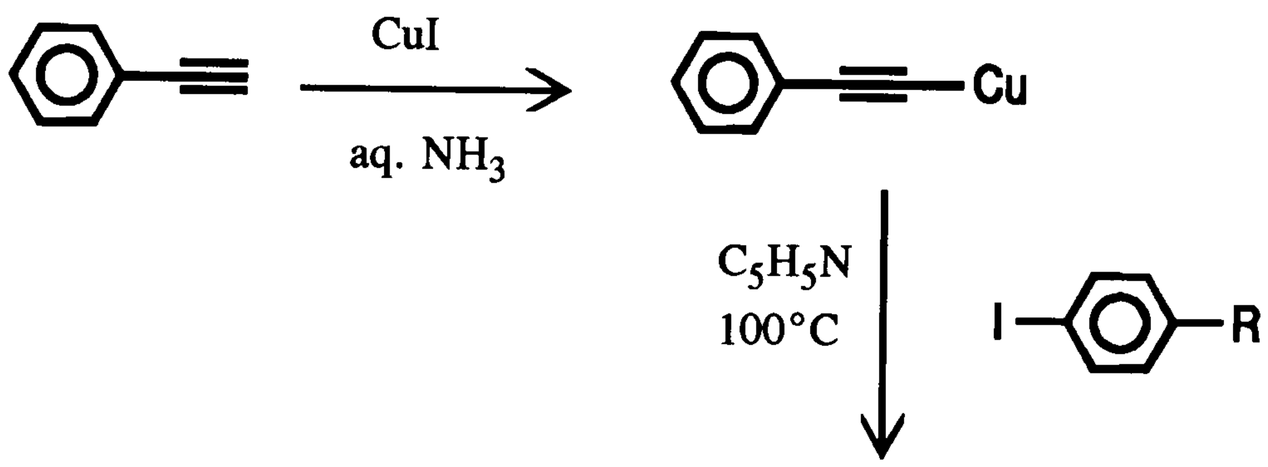
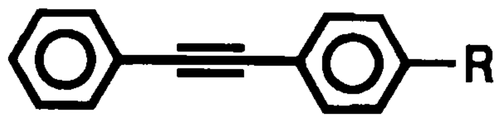
21. Austin W.B. Bilow N. Kelleghan W.J. Lau K.S.Y. *J. Org. Chem.* 1981 **46** 2280-2286

aqueous ammonia[22] or with copper *tert*-butoxide[23], reacts with aryl iodides in pyridine to give symmetrical or unsymmetrical diarylacetylenes[22].



Symmetrical diarylacetylene formation





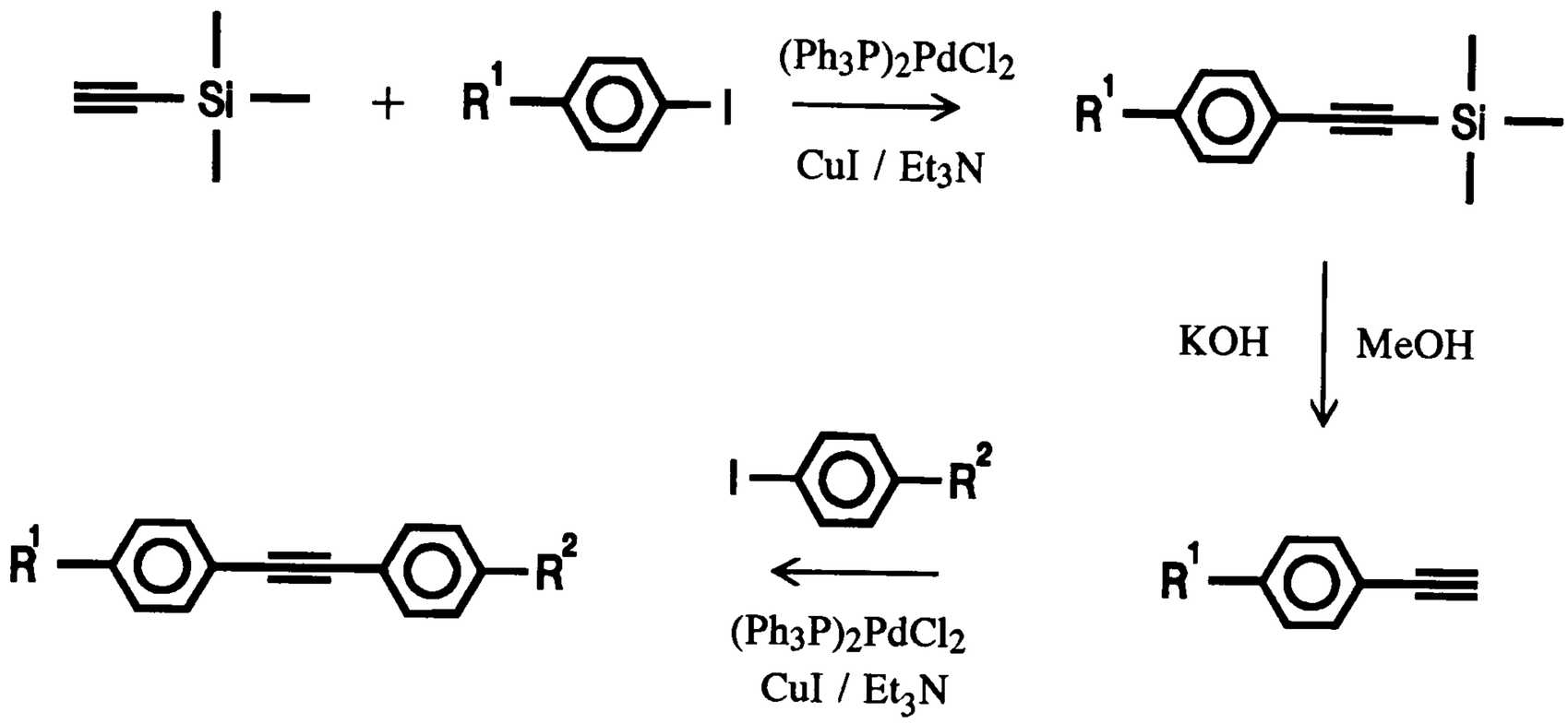
Unsymmetrical diarylacetylene formation

Other methods of producing unsymmetrical diarylacetylenes and monoarylacetylenes include acetylenes with protecting groups like 2-hydroxy-2-propyl[15] and trimethylsilyl[16,21,24]. (Iodoethynyl)trimethylsilane, formed from ethynyltrimethylsilane and iodine monochloride in methylene chloride[25], reacts with an aryl copper followed by mild alkali to produce a monoarylacetylene[24].

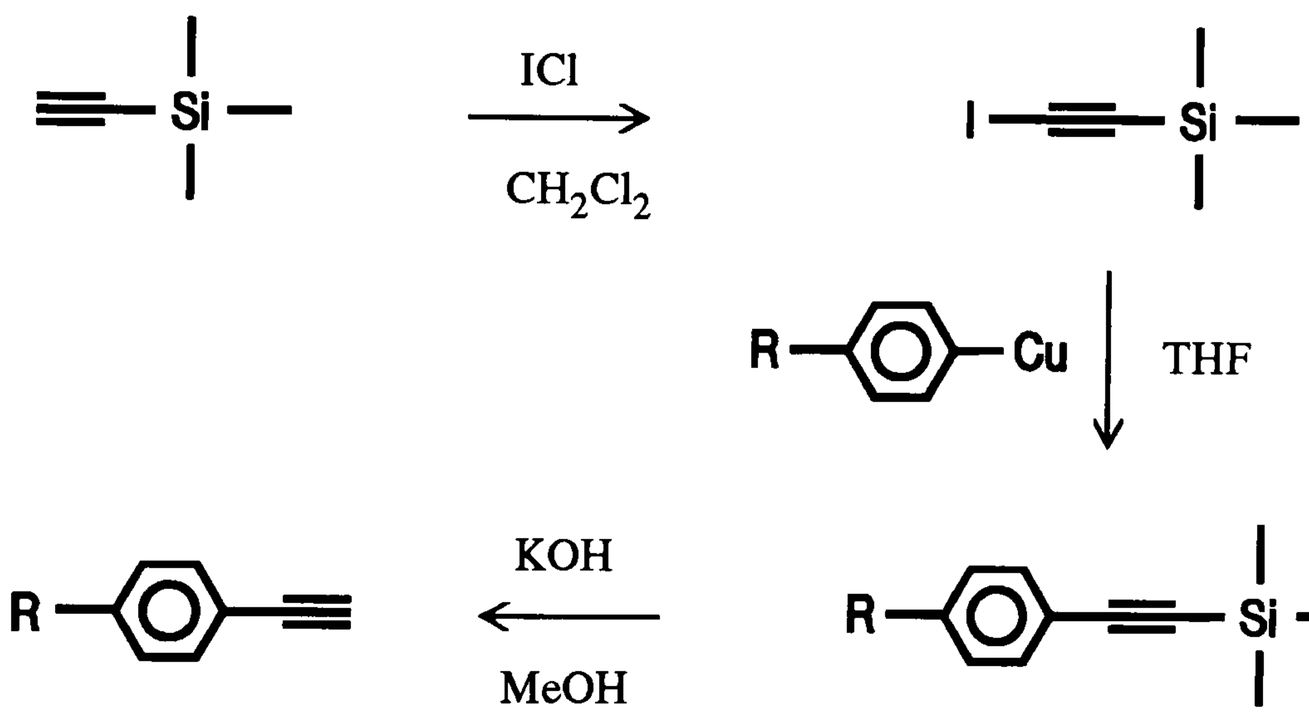
---

22. Stephens R.D. Castro C.E. *J. Org. Chem.* 1963 **28** 3313-3315
23. Tsuda T. Hashimoto T. Saegusa T. *J. Am. Chem. Soc.* 1972 **94** 658-659
24. Oliver R. Walton D.R.M. *Tetrahedron Letters* 1972 5209-5212
25. Walton D.R.M. Webb M.J. *J. Organometal. Chem.* 1972 **37** 41-43

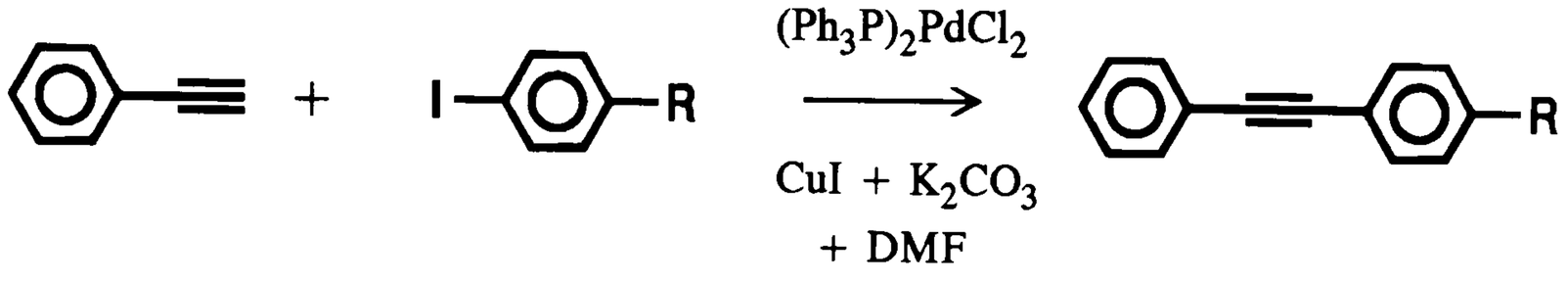
Diarylacetylene formation using a protecting group



Alternative route to monoarylacetylene

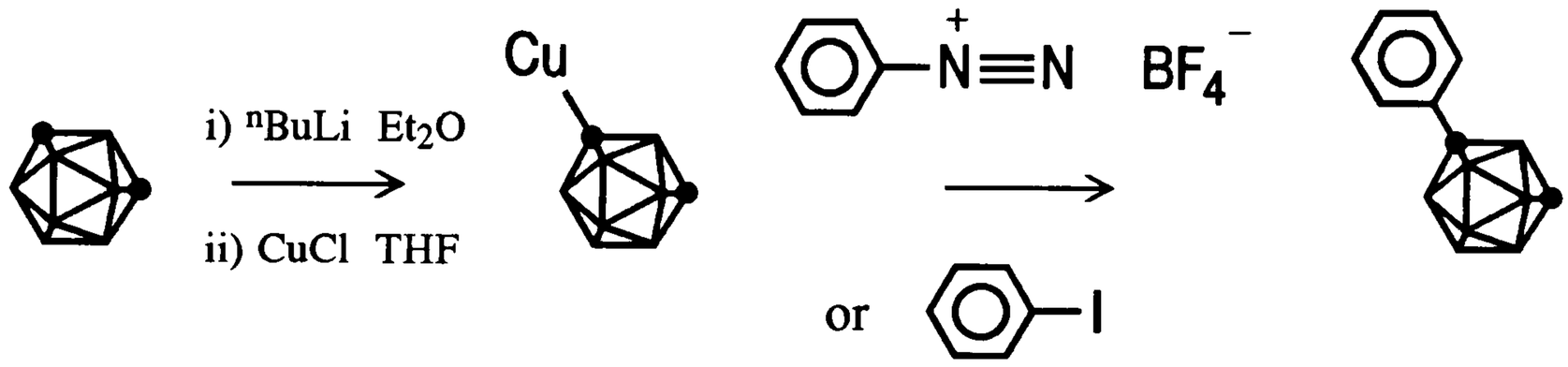


The reaction between terminal acetylenes and aryl iodides depends markedly on the aryl iodide used. For example 4-nitro-1-iodobenzene reacts with phenylacetylene in the presence of a palladium catalyst, copper iodide and potassium carbonate with dimethylformamide as solvent to give 4-nitrodiphenylacetylene in 96% yield whereas 4-methoxydiphenylacetylene is obtained in only 35% yield with 4-methoxy-1-iodobenzene instead of 4-nitro-1-iodobenzene[18].



96% yield with R = NO_2 35% yield with R = OMe

1-aryl-*ortho*-, -*meta*- and -*para*-carboranes can also be produced from their parent carboranes. The parent carborane is converted into a copper derivative which reacts with either an aryldiazonium tetrafluoroborate[26,27] or phenyl iodide[28] to form the monoarylcarborane.



Carbon-aryl-*ortho*-carboranes can also be made from lithiocarborane with hexafluorobenzene. The pentafluorophenyl carborane, formed from lithiocarborane and hexafluorobenzene, is then attacked at the *para* position of the pentafluorophenyl group by lithiocarborane in preference to hexafluorobenzene to yield a compound with two carborane cages[29,30]. With chloropentafluorobenzene, a diaryl-carborane is produced[30].

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27. Kovredov A.I. Shaugumbekova Zh.S. Kazantsev V.A. Zakharkin L.I. *J. Gen. Chem. U.S.S.R.* 1986 **56** 2045-2049
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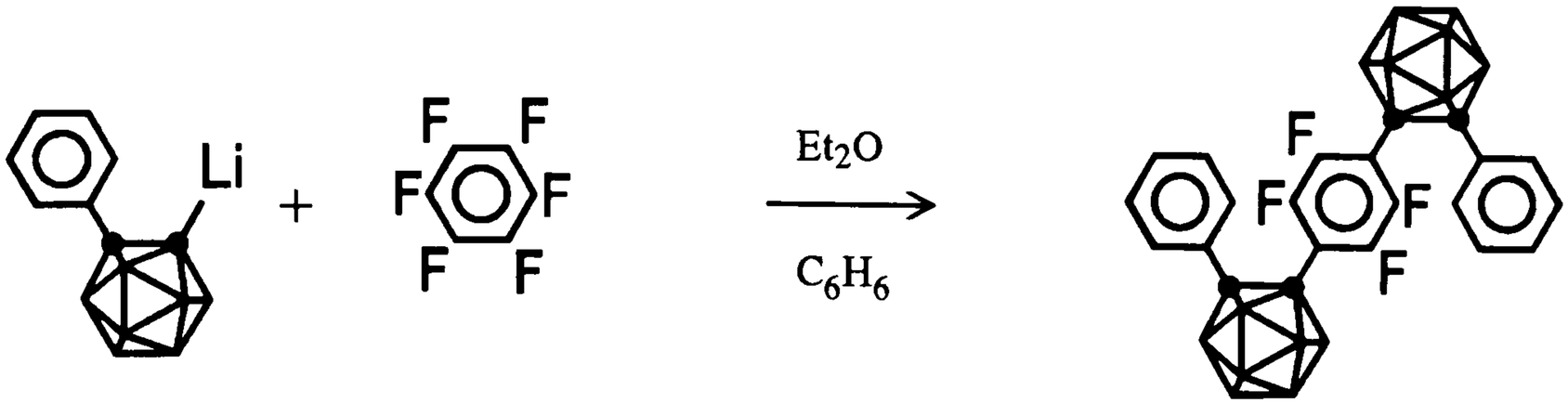
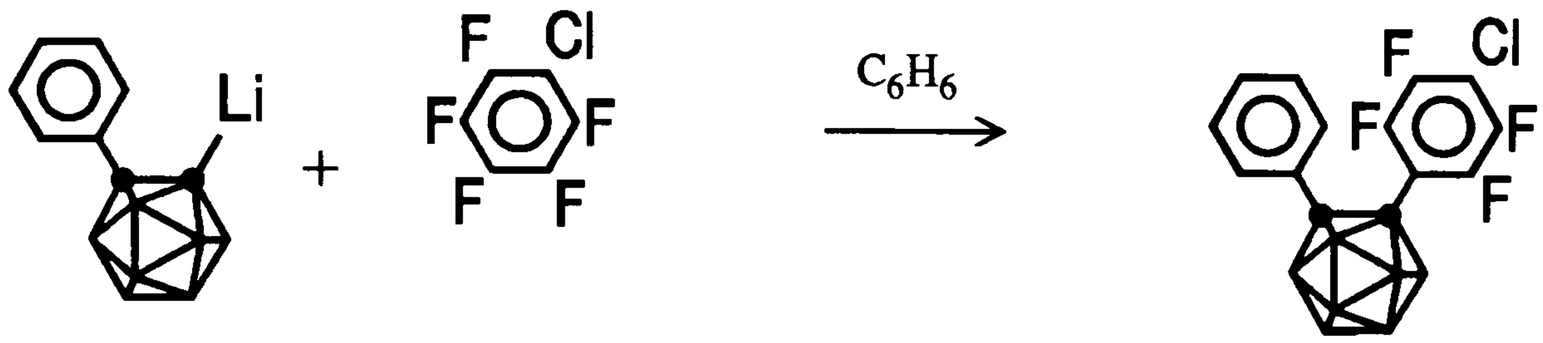
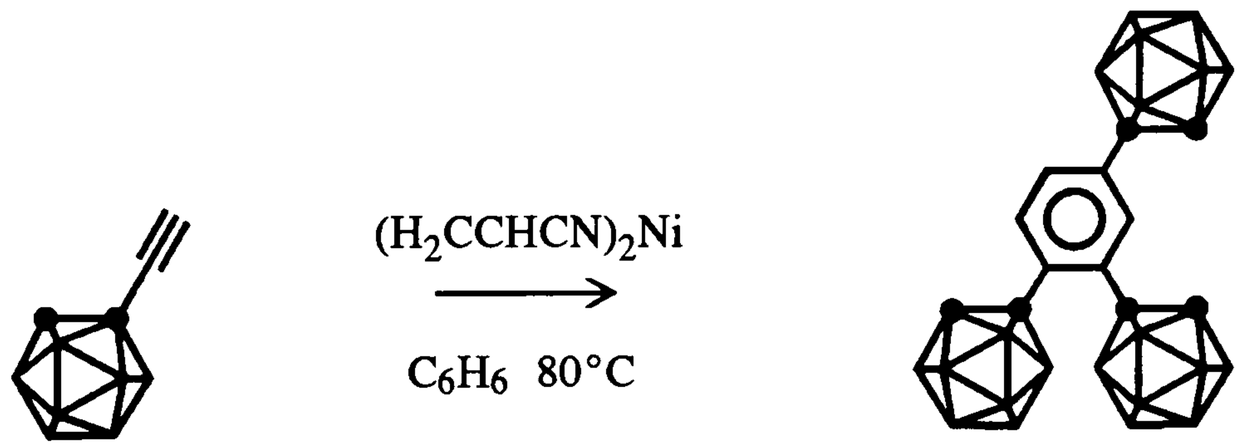




Catalytic trimerization of 1-ethynyl-*ortho*-carborane, which can be produced from the copper derivative of *ortho*-carborane and (bromoethynyl)trimethylsilane[31,32], produced a 1,2,4-trisubstituted benzene with carborane cages as substituents in 85% yield[33].



1-aryl- and 1,2-diaryl-*meta*-carboranes can be obtained by thermal isomerization of 1-aryl- and 1,2-diaryl-*ortho*-carboranes at 400-450°C if the substituents are not affected at these temperatures[3,34].

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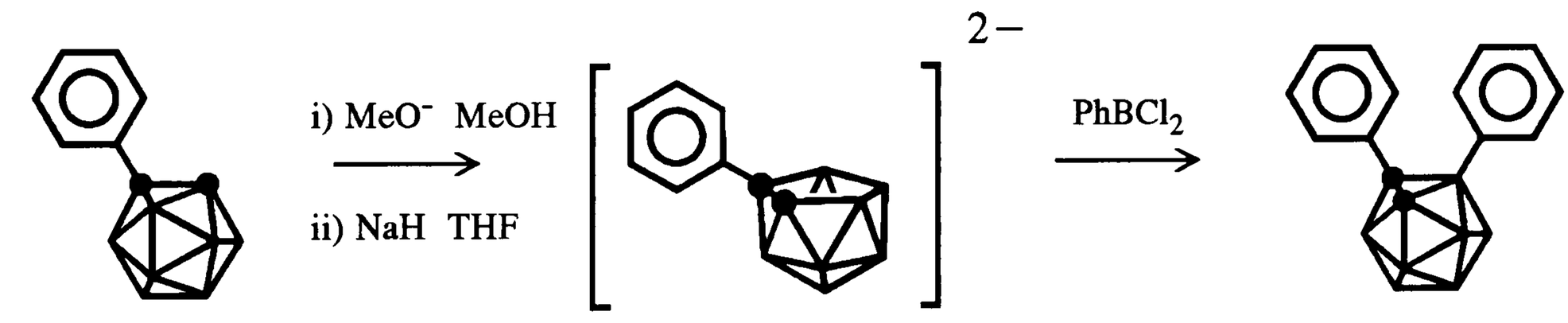
CHEMICAL PROPERTIES OF CARBON-ARYL CARBORANES

Nitration of 1-phenyl-*ortho*-carborane gave a mixture of 1-nitrophenyl-*ortho*-carborane isomers with the nitro group at *ortho*, *meta* or *para* positions of the aromatic ring and the ratio of isomers is 5:25:70 for *ortho* : *meta* : *para*[35]. The isomer ratio is typical of a radical, not electrophilic, substitution reaction. Halogenation of carbon-aryl carboranes occurs at the cage to give products with boron-halogen bonds[36,37,38]. Iodination of 1-phenyl-*ortho*-carborane is described in detail in Chapter 4. Acylation of the aromatic ring of 1-phenyl-*ortho*-carborane does not proceed at all even under severe conditions[39].

Nucleophiles degrade the cage of carbon-aryl carboranes as in parent carboranes. 1,3-diphenyl-*ortho*-carborane can be produced by insertion of the *nido*-dicarbaundecaborate anion, from 1-phenyl-*ortho*-carborane and sodium methoxide, with phenylboron dichloride[40].



1-C_6H_5-
1,2-$C_2B_{10}H_{11}$

C_6H_5-
7,8-$C_2B_9H_{11}^{2-}$

1,3-$(C_6H_5)_2$-
1,2-$C_2B_{10}H_{10}$

35. Zakharkin L.I. Kalinin V.N. *Dokl. Akad. Nauk. S.S.S.R.* 1965 **164** 577-580 (Russ) **CA**63:18134f
36. Stanko V.I. Brattsev V.A. Vostrikova T.N. Danilova G.N. *J. Gen. Chem. U.S.S.R.* 1968 **38** 1300-1303
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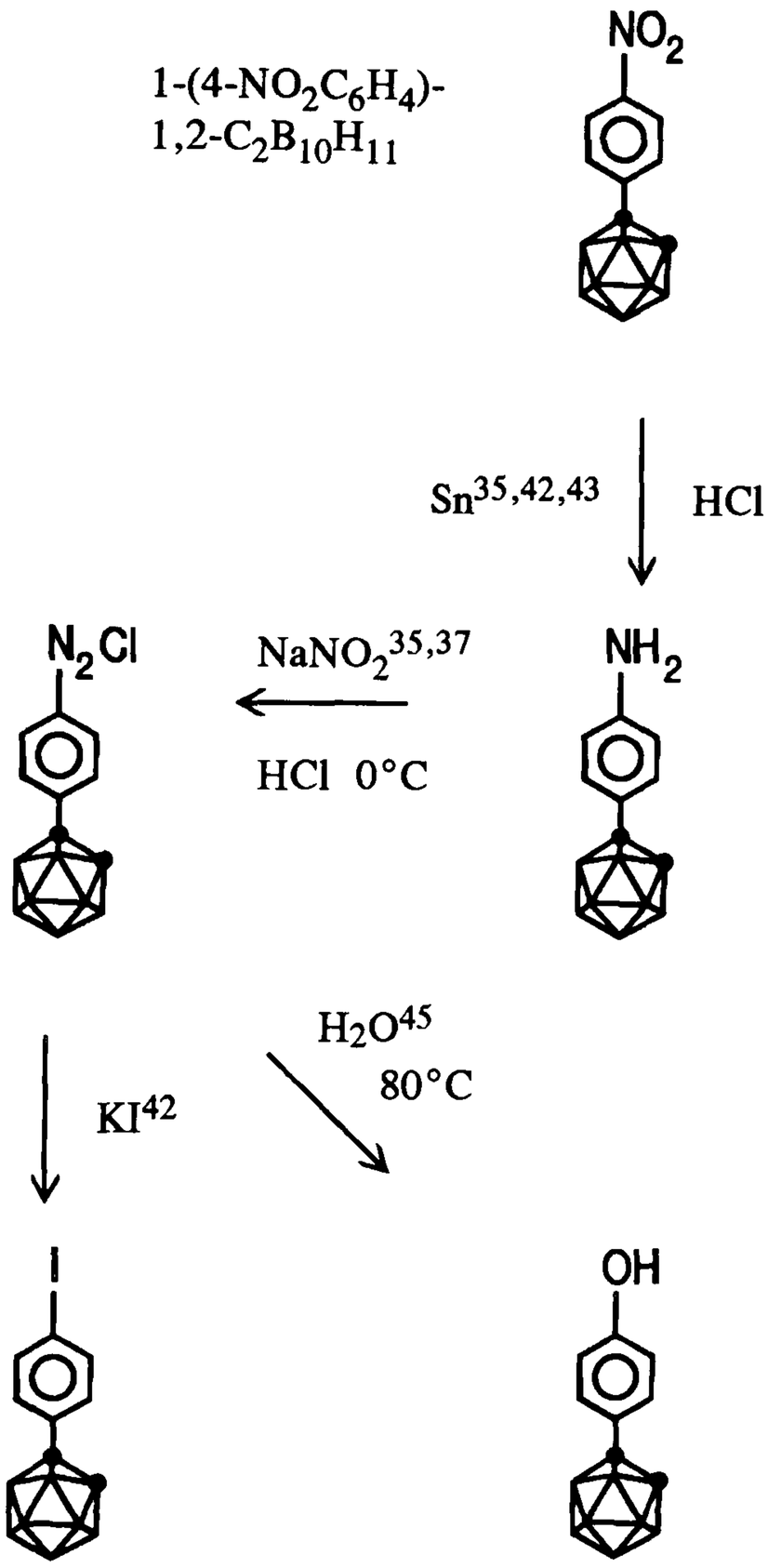
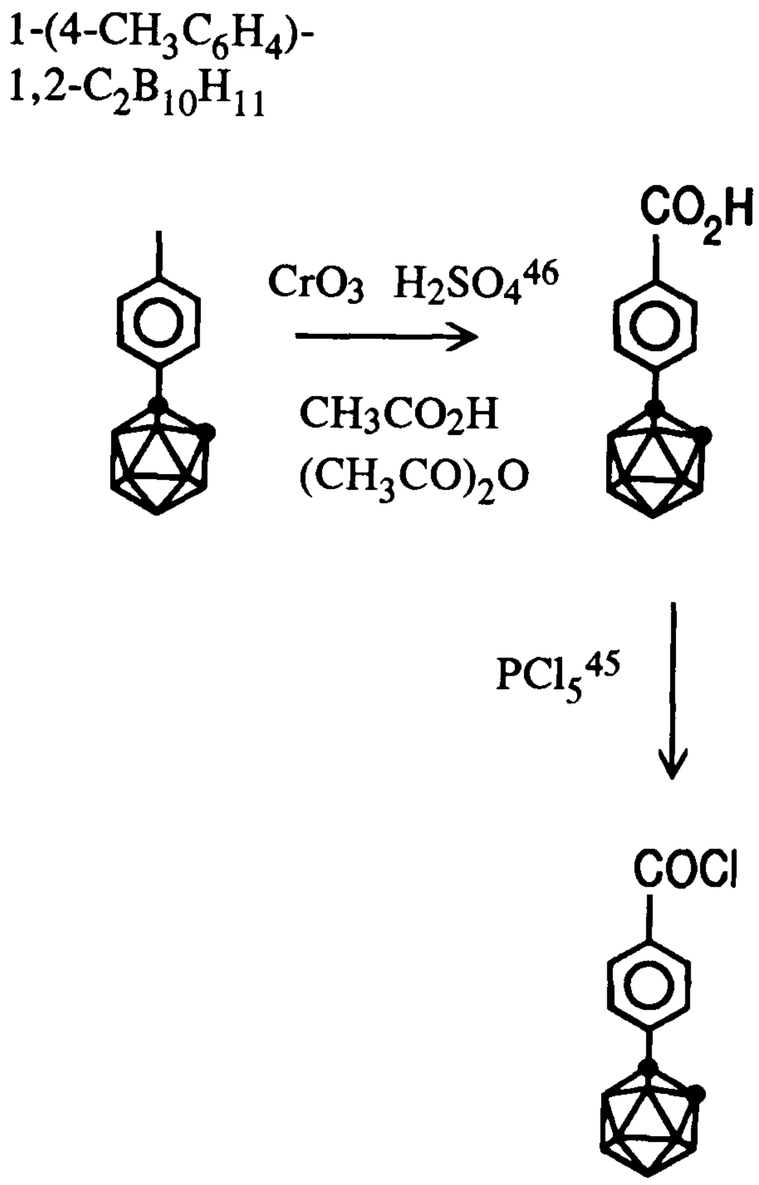
39. Zakharkin L.I. Kalinin V.N. *J. Org. Chem. U.S.S.R.* 1987 **23** 1513-1516
40. Hawthorne M.F. Wegner P.A. *J. Am. Chem. Soc.* 1968 **90** 896-901

Some chemical properties of 1-aryl- and 1,2-diarylcarboranes are like the chemical properties of other substituted benzenes[41]. The two schemes below show the similarities.





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42. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1965 2173-2175
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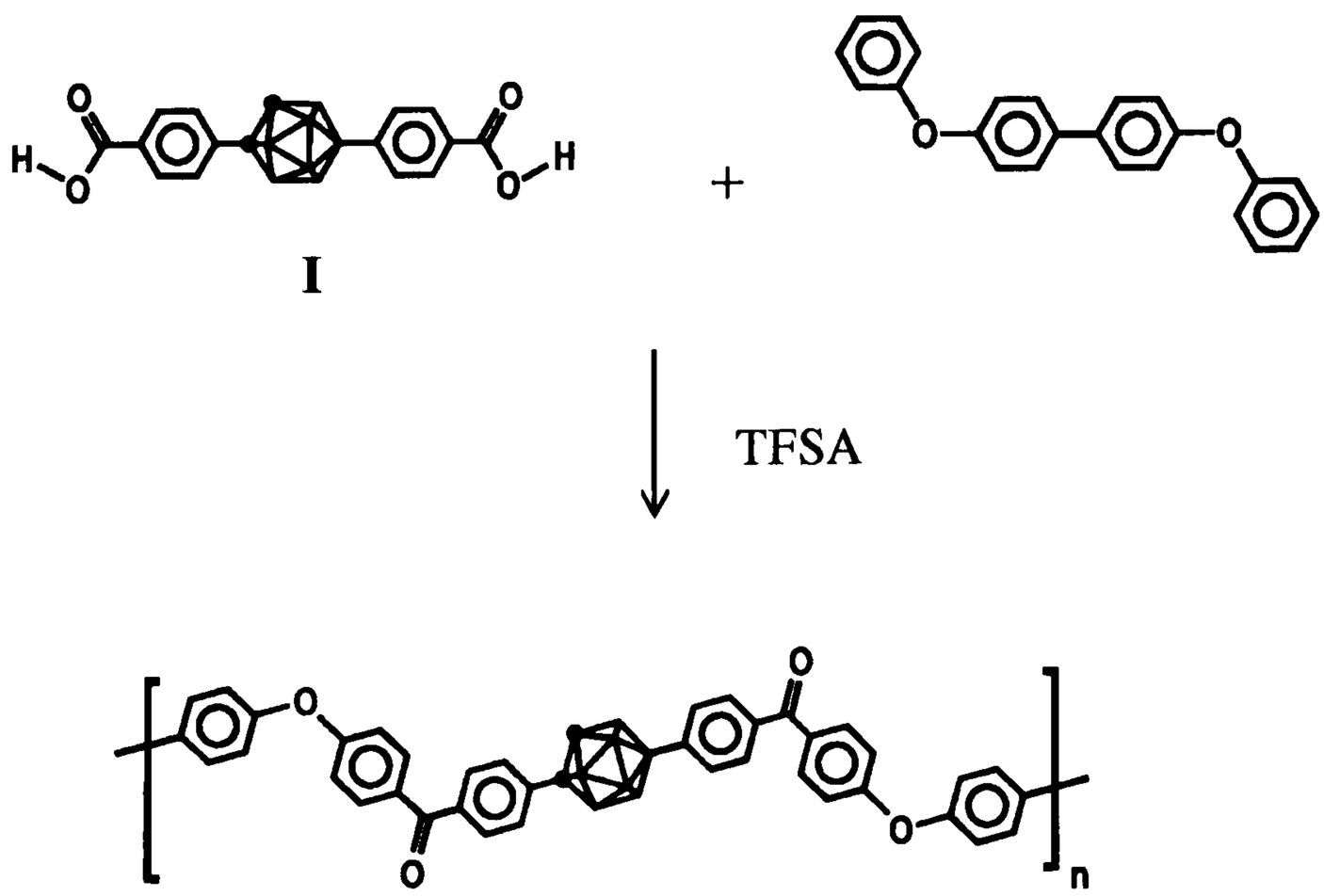
MONOMER SYNTHESES

Two monomers, 1,2-bis(4-phenoxyphenyl)-*ortho*-carborane and 1,2-bis(4-carboxyphenyl)-*ortho*-carborane, have been produced for CPEK formation. The target monomers are the *meta* analogues, 1,7-bis(4-phenoxyphenyl)-*meta*-carborane and 1,7-bis(4-carboxyphenyl)-*meta*-carborane, as *meta*-carborane itself is thermally and chemically more stable than *ortho*-carborane.

Another monomer targeted was 1,12-bis(4-carboxyphenyl)-*ortho*-carborane (**I**) where one aryl group is attached to a cage boron and another to a cage carbon. The attraction was that the CPEK that could be formed from this monomer was expected to be more linear than the CPEKs already made. The synthesis of 1,12-bis(4-carboxyphenyl)-*para*-carborane was not attempted as *para*-carborane itself was not commercially available and very low yields of *para*-carborane derivatives are obtained from thermal isomerization of *ortho*- or *meta*-carborane derivatives.

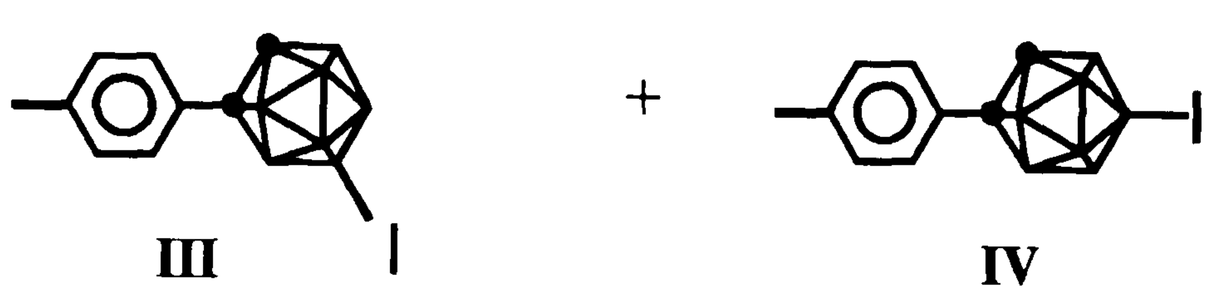


I

Possible CPEK formation

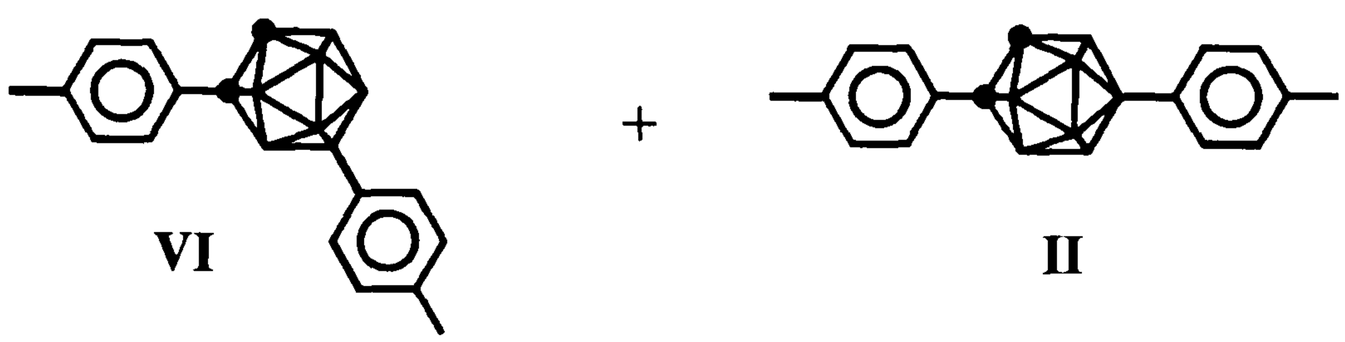
1,12-bis(4-phenoxyphenyl)-*ortho*-carborane is not expected to be a suitable monomer as shown by the model reaction of 9-(4-phenoxyphenyl)-*ortho*-carborane in Chapter 5.

The synthesis of 1,12-bis(4-methylphenyl)-*ortho*-carborane (**II**) was attempted by the two routes shown below. Route **A**, the formation of the diaryl carboranes from 9- and 12-iodo-1-(4-methylphenyl)-*ortho*-carborane isomers (**III** and **IV**) and 4-methylphenylmagnesium iodide in the presence of palladium catalyst, was unsuccessful.



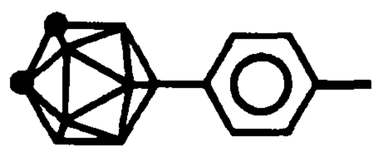
III + **IV**

[Route A] $(Ph_3P)_2PdCl_2$, Et_2O ✕ MgI



VI + **II**

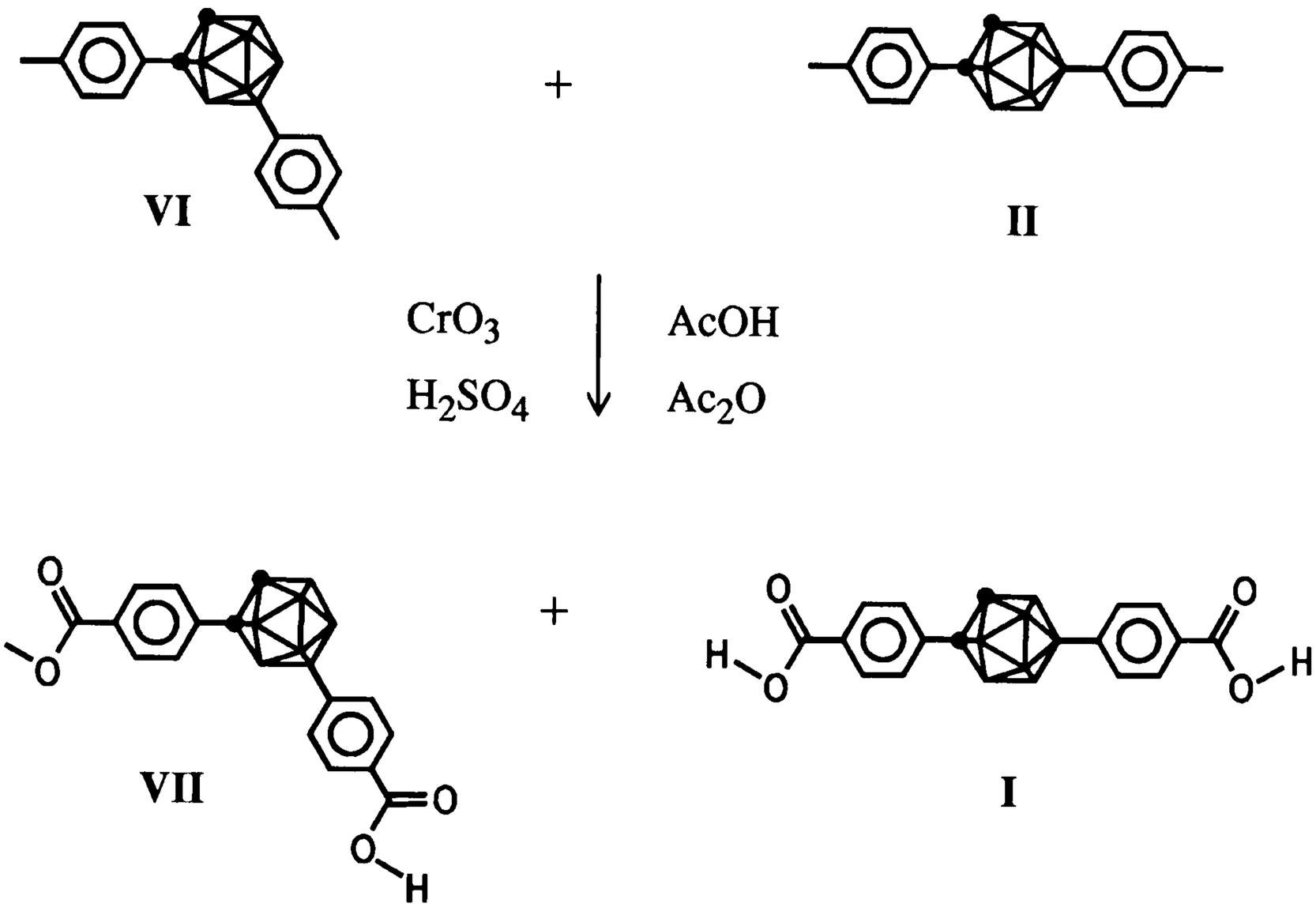
[Route B] i) ^nBuLi Et_2O; ii) CuCl THF; iii) $N\equiv N^+ BF_4^-$



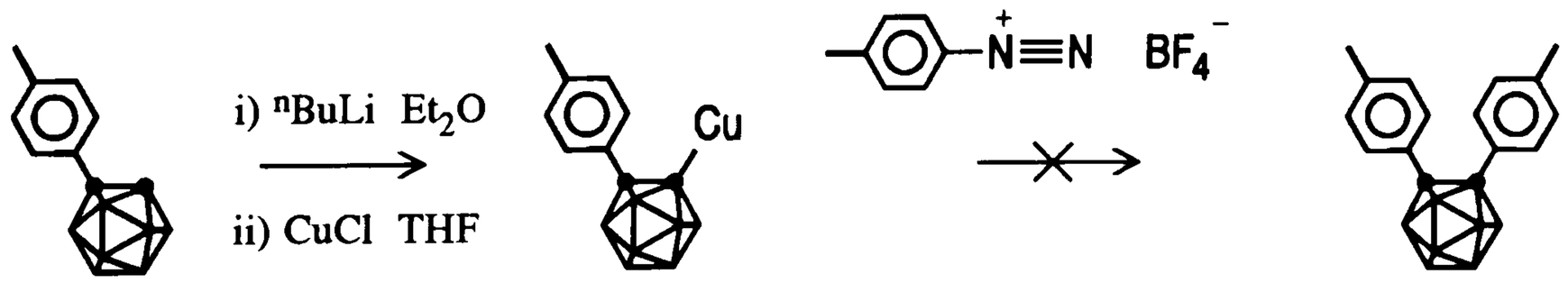
V

Before route **B** was attempted, 1-(4-methylphenyl)-*ortho*-carborane was successfully made from the copper derivative of *ortho*-carborane and 4-methylphenyldiazonium tetrafluoroborate. The same method was carried out on 9-(4-methylphenyl)-*ortho*-carborane (**V**) which produced the first known 1,9- and 1,12-diaryl-*ortho*-carborane isomers (**VI** and **II**). A small amount of pure 1,12-bis(4-methylphenyl)-*ortho*-carborane (**II**) was obtained by fractional crystallization of the isomeric mixture.

Oxidation of the 1,9- and 1,12-bis(4-methylphenyl)-*ortho*-carborane isomers gave the expected 1,9- and 1,12-bis(4-carboxyphenyl)-*ortho*-carborane isomers (**VII** and **I**) which are potential monomers for CPEK formation. The separation of these isomers were not attempted as model polymerization studies using the mixture were of higher priority.

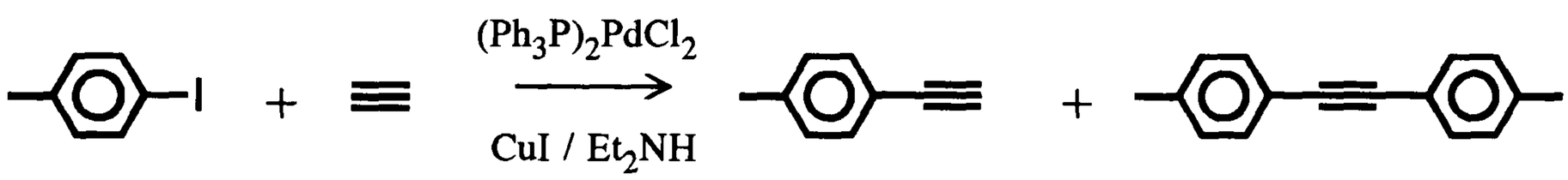


For the synthesis of 1,7-bis(4-methylphenyl)-*meta*-carborane, 1,2-bis(4-methylphenyl)-*ortho*-carborane (**VIII**) was chosen as it could be isomerized and then oxidised to the required *meta* dicarboxylic acid[3]. The formation of 1,2-bis(4-methylphenyl)-*ortho*-carborane was attempted from the copper derivative of 1-(4-methylphenyl)-*ortho*-carborane and 4-methylphenyldiazonium tetrafluoroborate. This was unsuccessful, probably due to the steric influence of the first aryl substituent on the reaction site.



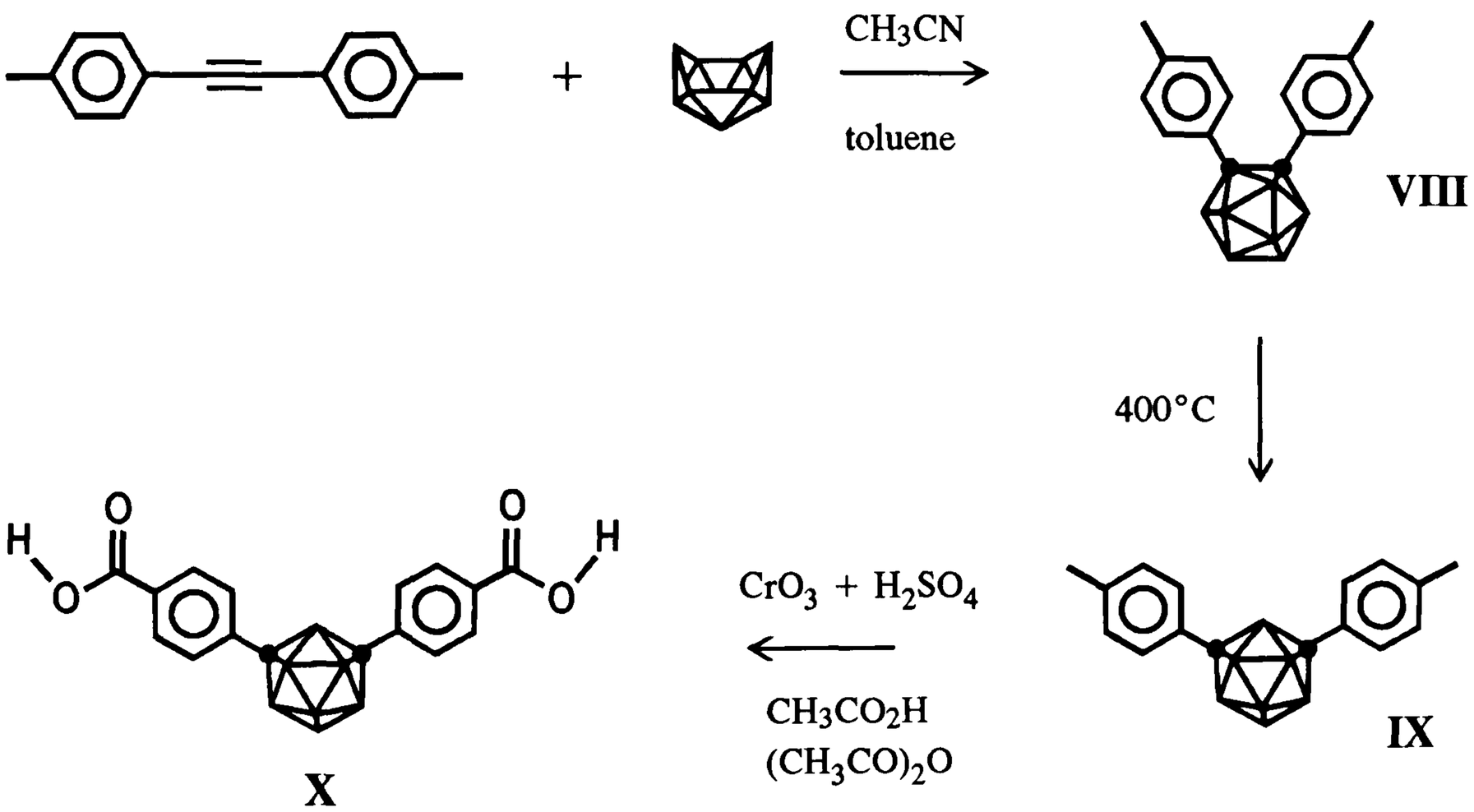
VIII

Bis(4-methylphenyl)acetylene, required for the formation of 1,2-bis(4-methylphenyl)-*ortho*-carborane, was made from two methods. One preparation was the simple coupling reaction[13] between acetylene and 4-iodotoluene in the presence of a catalytic mixture of copper (I) iodide and bis(triphenylphosphino)palladium dichloride in diethylamine. Only 27% yield of the diarylacetylene was obtained, the major product was an oil identified as crude 4-ethynyltoluene by infrared spectroscopy. The yield of the diarylacetylene might be increased if the acetylene flow was substantially reduced. The method using 4-methylphenylethynyl copper, formed from copper (I) iodide in aqueous ammonia with 4-ethynyltoluene, and 4-iodotoluene in refluxing pyridine gave the diarylacetylene in good yield.

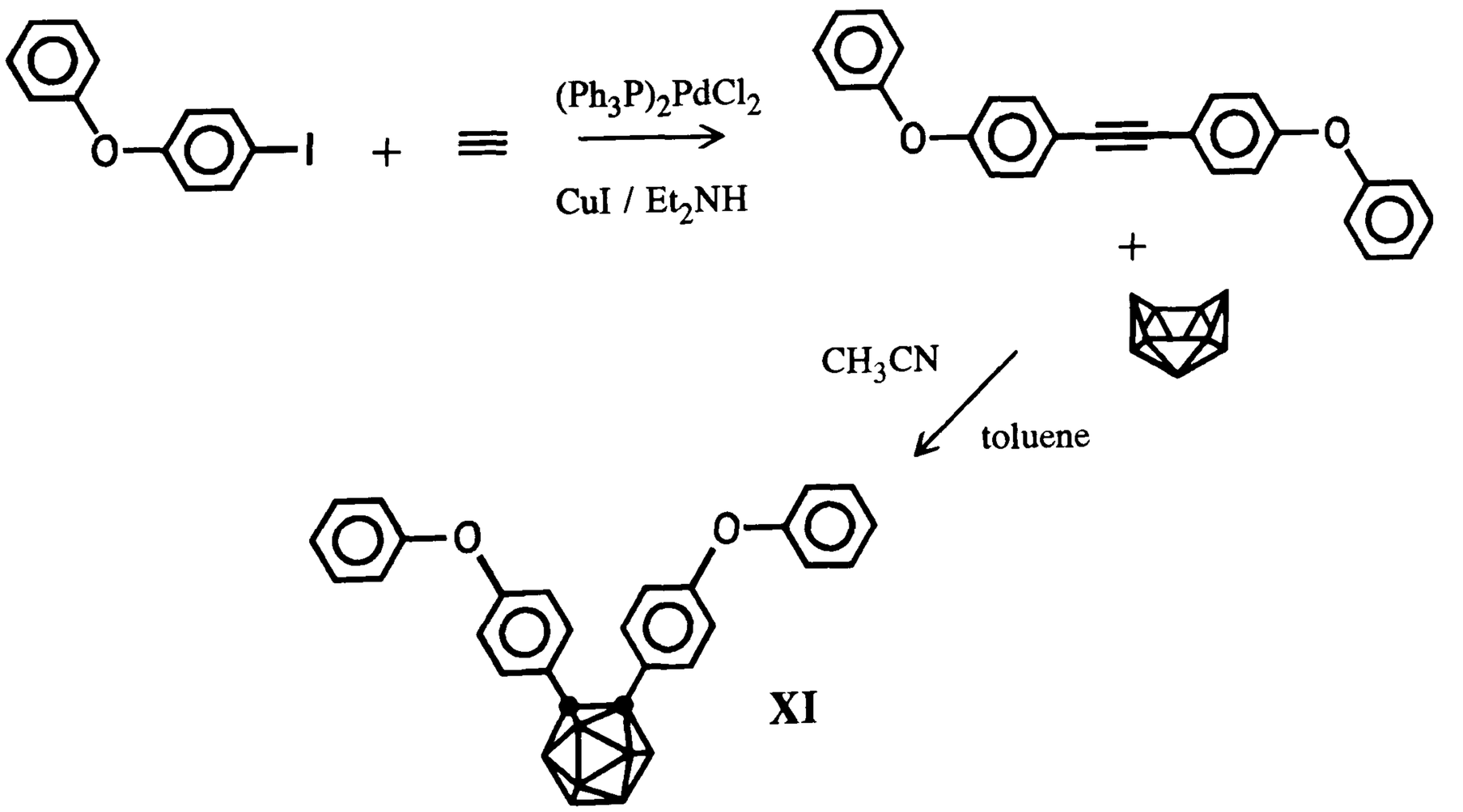


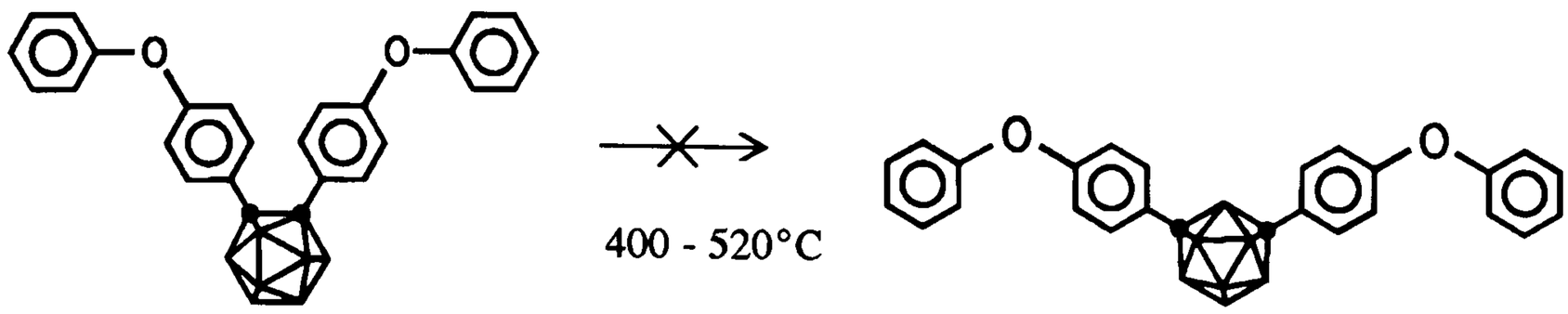
Bis(4-methylphenyl)acetylene reacted with 6,9-bis(acetonitrile)-decaborane in refluxing toluene to give the expected 1,2-bis(4-methylphenyl)-*ortho*-carborane (**VIII**) which was heated to 400°C for 24 hours to yield a mixture of the unchanged *ortho* isomer and 1,7-bis(4-methylphenyl)-*meta*-carborane (**IX**). The

separation of the isomers was carried out by several runs of column chromatography in hexane instead of controlled degradation as the *ortho* isomer is also useful for CPEK formation. The diaryl-*meta*-carborane was oxidized to the monomer, 1,7-bis(4-carboxyphenyl)-*meta*-carborane (**X**), using chromium trioxide and sulphuric acid.



A similar route for the synthesis of 1,7-bis(4-phenoxyphenyl)-*meta*-carborane (**XII**) was envisaged as shown below. Bis(4-phenoxyphenyl)acetylene, easily obtained from acetylene and 4-iododiphenyl ether, gave 1,2-bis(4-phenoxyphenyl)-*ortho*-carborane (**XI**) with 6,9-bis(acetonitrile)-decaborane.

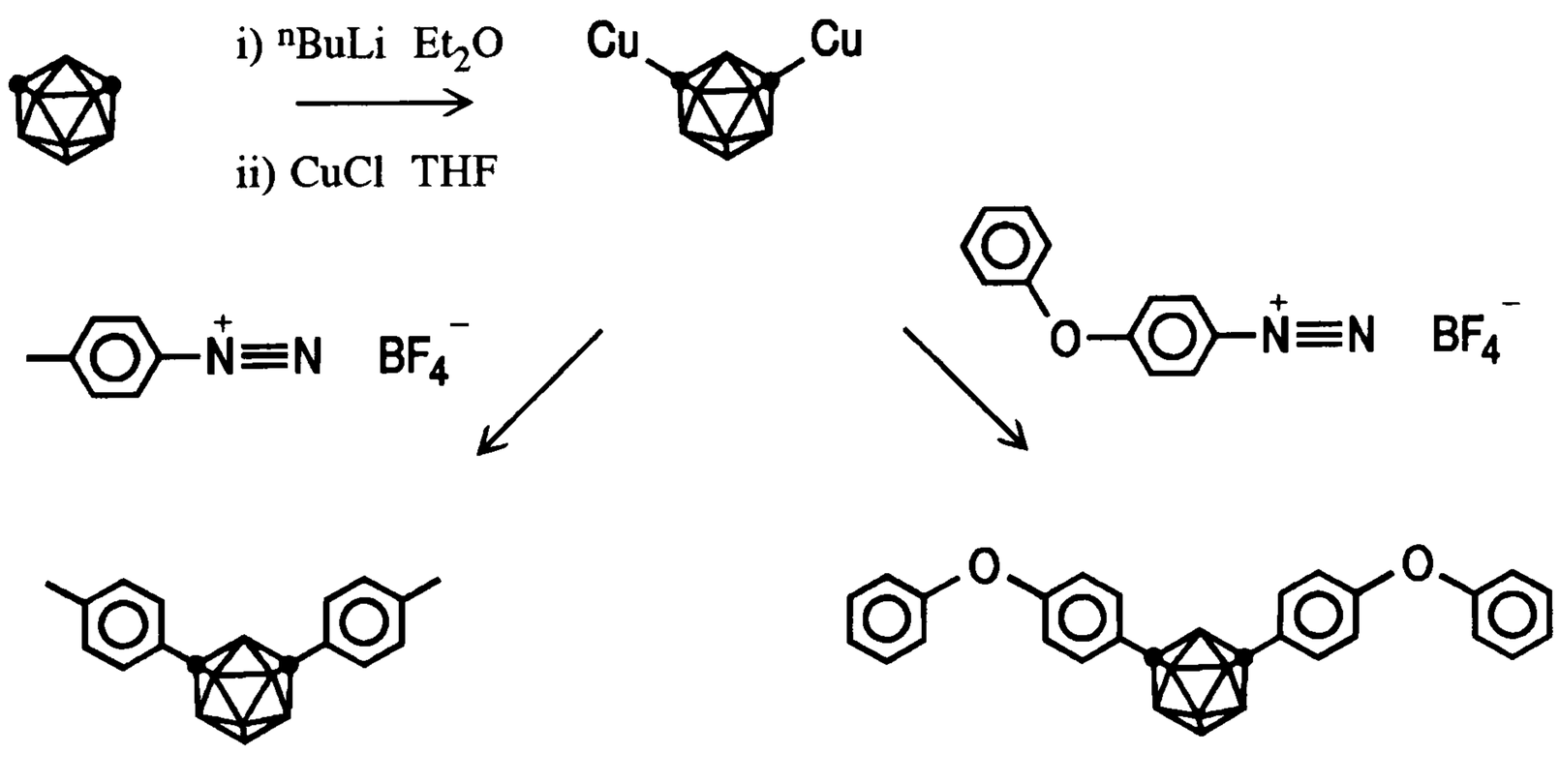




XI **XII**

However the thermal isomerization of the *ortho* derivative proved to be unsuccessful, the compound was unaffected at 400°C and 460°C and formed an insoluble glassy mass at 520°C which is probably "polycarborane" by hydrogen abstraction and ether cleavage at temperatures over 500°C[47].

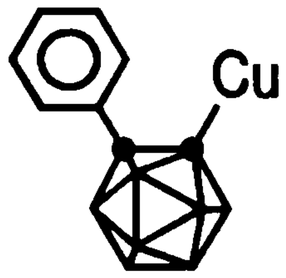
As 1,2-bis(4-methylphenyl)-*ortho*-carborane could not be produced from *ortho*-carborane, 1,7-diaryl-*meta*-carboranes were not expected to be formed from *meta*-carborane. On the contrary, *meta*-carborane gave 1,7-diaryl-*meta*-carboranes by treating the dicopper derivative of *meta*-carborane with two equimolar amounts of aryldiazonium tetrafluoroborates. 1,7-bis(4-methylphenyl)-*meta*-carborane (**IX**) and the previously unknown 1,7-bis(4-phenoxyphenyl)-*meta*-carborane (**XII**) were obtained by this facile method.



IX **XII**

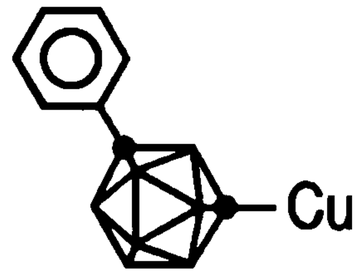
47. Zakharkin L.I. Kalinin V.N. Balykova T.N. Gribkova P.N. Korshak V.V. *J. Gen. Chem. U.S.S.R.* 1973 **43** 2249-2254

The steric effect of the aryl group on the second reaction site probably explains why 1,2-diaryl-*ortho*-carboranes could not be produced from *ortho*-carborane unlike the *meta* analogues where the aryl group is too distant to cause a steric effect on the second reaction site.



ortho

steric effect of aryl group on the reactive site prevents formation of diarylcarborane.

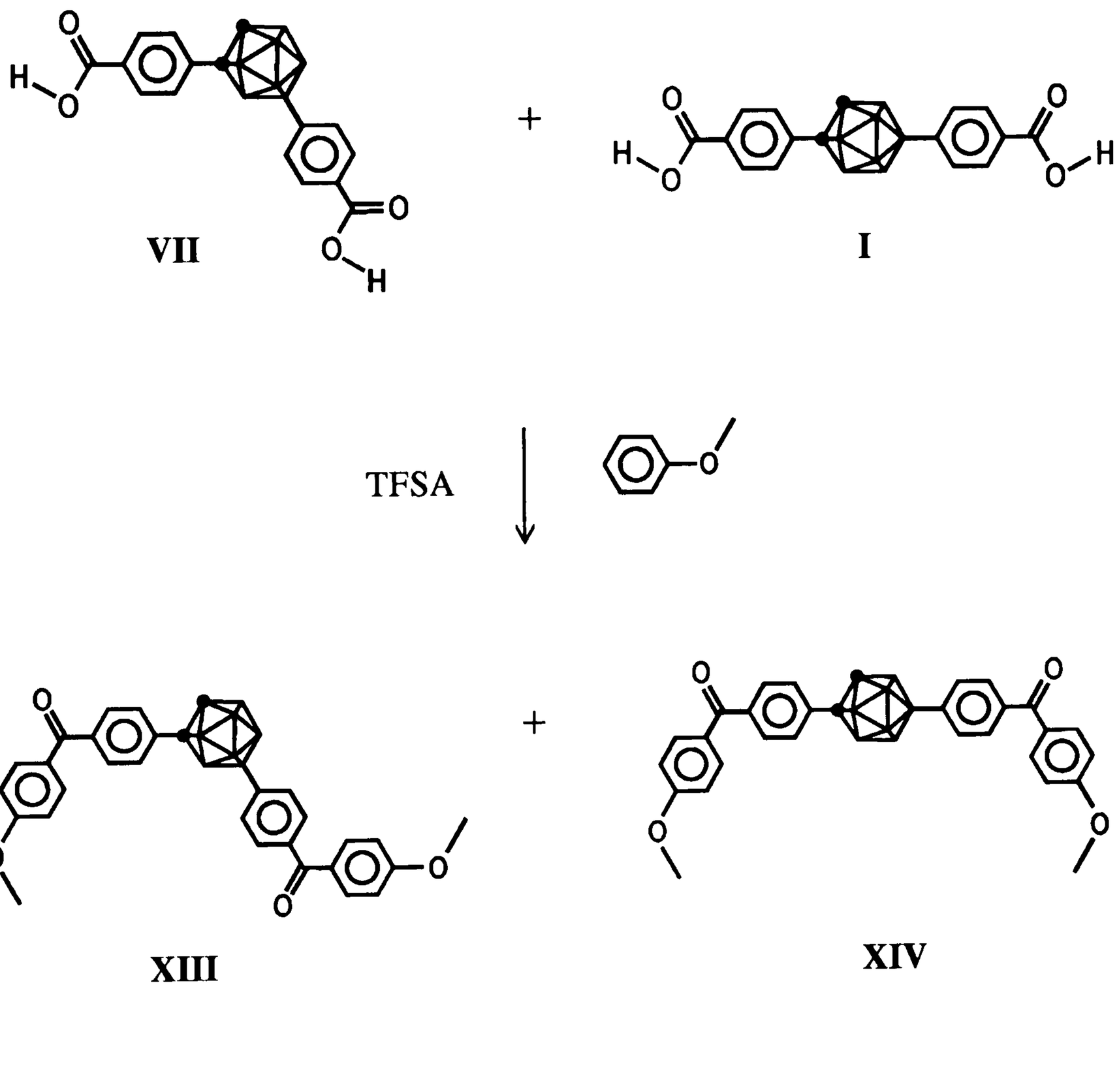


meta

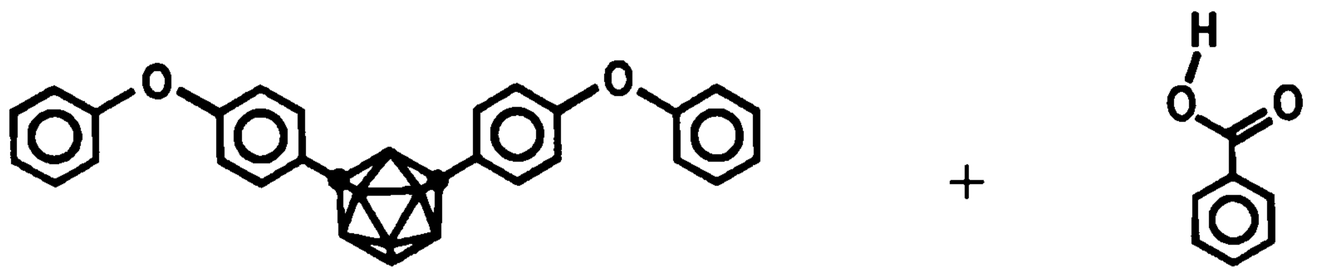
no steric effect of aryl group on the reaction site enables diarylcarborane formation.

MODEL REACTIONS

A mixture of 1,9- and 1,12-bis(4-carboxyphenyl)-*ortho*-carborane isomers (**VII** and **I**) with anisole in TFSA gave insoluble products. The elemental analysis, mass spectrum and infrared spectrum of the mixture of products pointed to the expected 1,9- and 1,12-bis(4′-methoxy-4-benzoylphenyl)-*ortho*-carborane isomers (**XIII** and **XIV**) but ^{13}C n.m.r. information is required for confirmation.

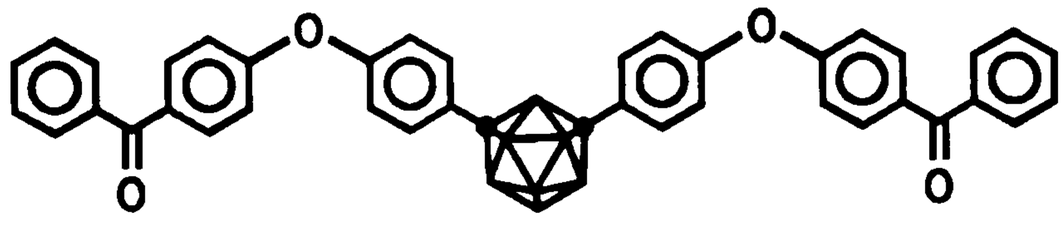


1,7-bis(4-phenoxyphenyl)-*meta*-carborane (**XII**) and two equimolar amounts of benzoic acid in TFSA gave the expected product 1,7-bis(4′-benzoyl-4-phenoxyphenyl)-*meta*-carborane (**XV**). Likewise 1,7-bis(4-carboxyphenyl)-*meta*-carborane (**X**) and two equimolar amounts of anisole in TFSA produced 1,7-bis(4′-methoxy-4-benzoylphenyl)-*meta*-carborane (**XVI**).

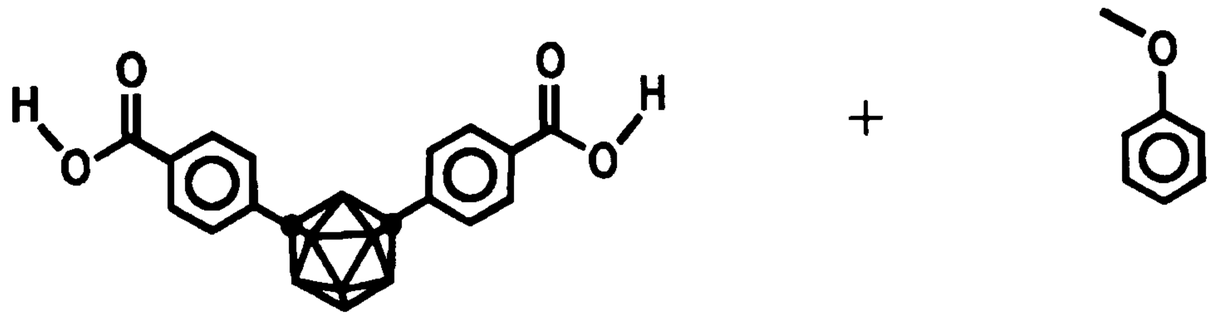


XII

TFSA

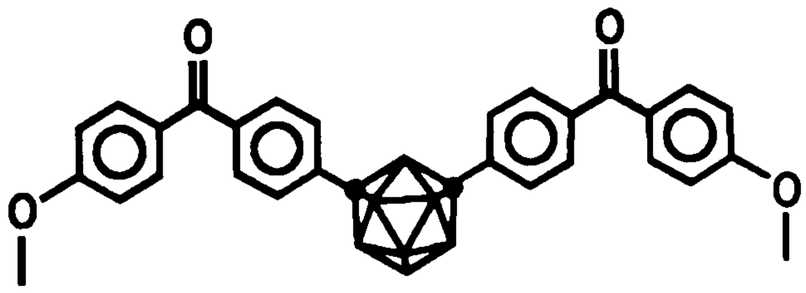


XV



X

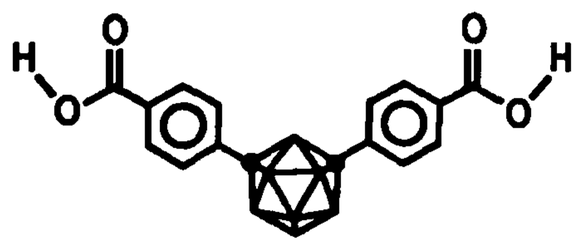
TFSA



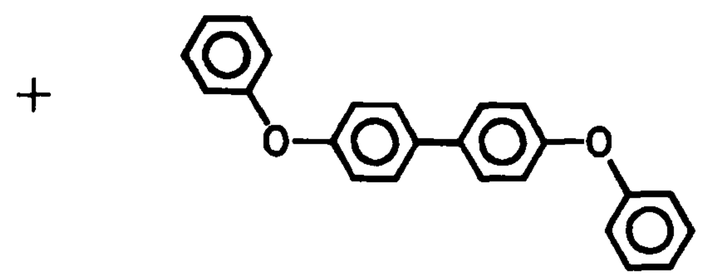
XVI

CPEK FORMATION

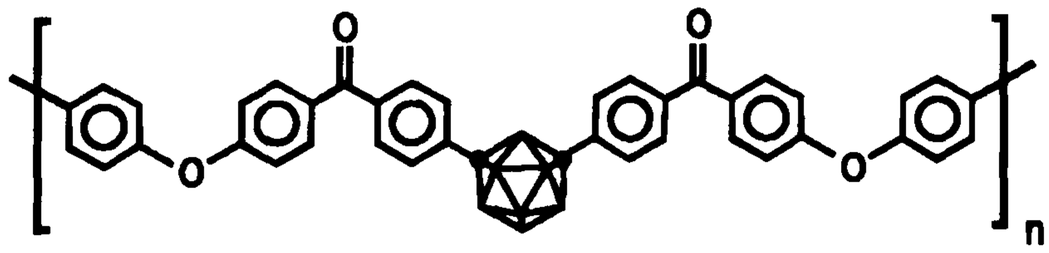
A CPEK (**XVII**) from 1,7-bis(4-carboxyphenyl)-*meta*-carborane (**X**) and 4,4′-diphenoxybiphenyl in TFSA has been made and characterized by elemental analysis, infrared, 1H and 13C n.m.r. spectroscopy but techniques used for characterizing polymers like differential scanning calorimetry (D.S.C.), gel permeation chromatography (G.P.C.) and thermogravimetric analysis (T.G.A.) have yet to be applied[48].



X



TFSA

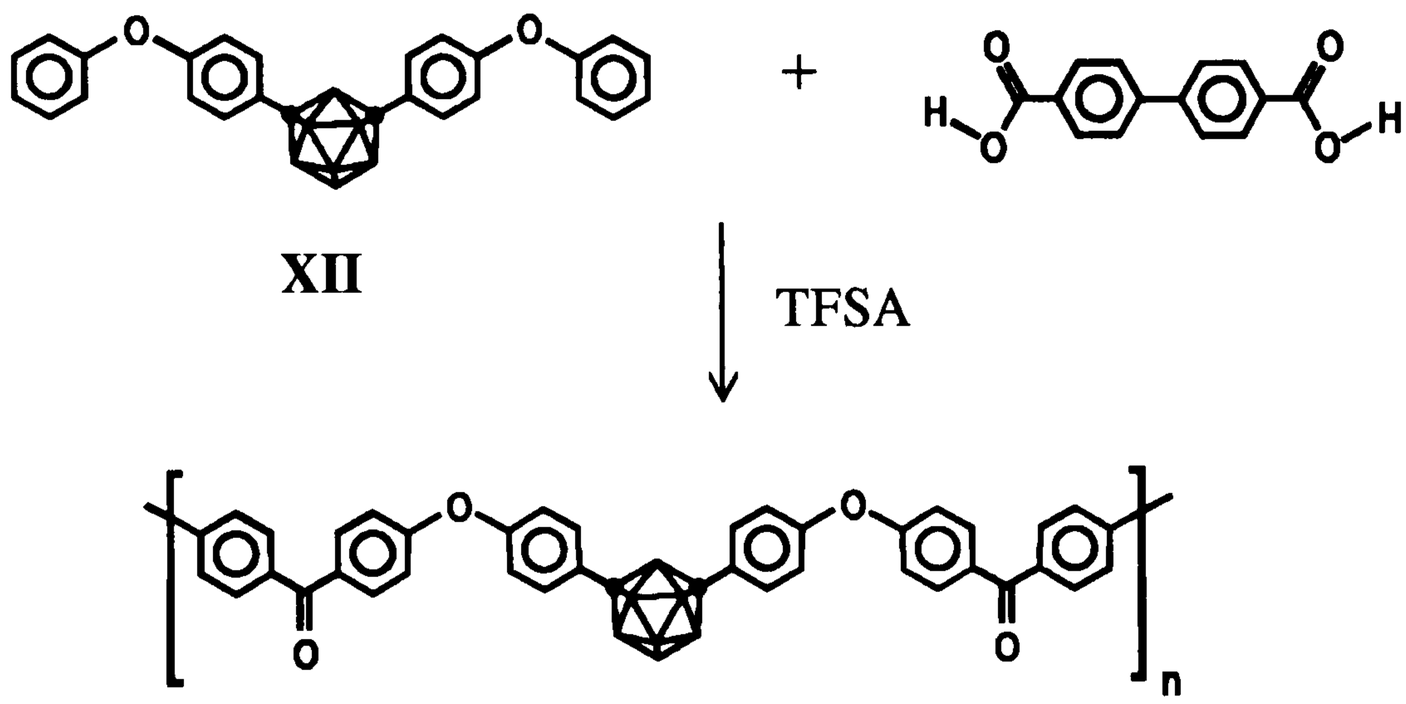


XVII

48. Stephenson I.R. "Novel Polymer and Derivative Chemistry of Icosahedral Carboranes" Ph.D. Thesis University of Durham Durham 1988 p127-139

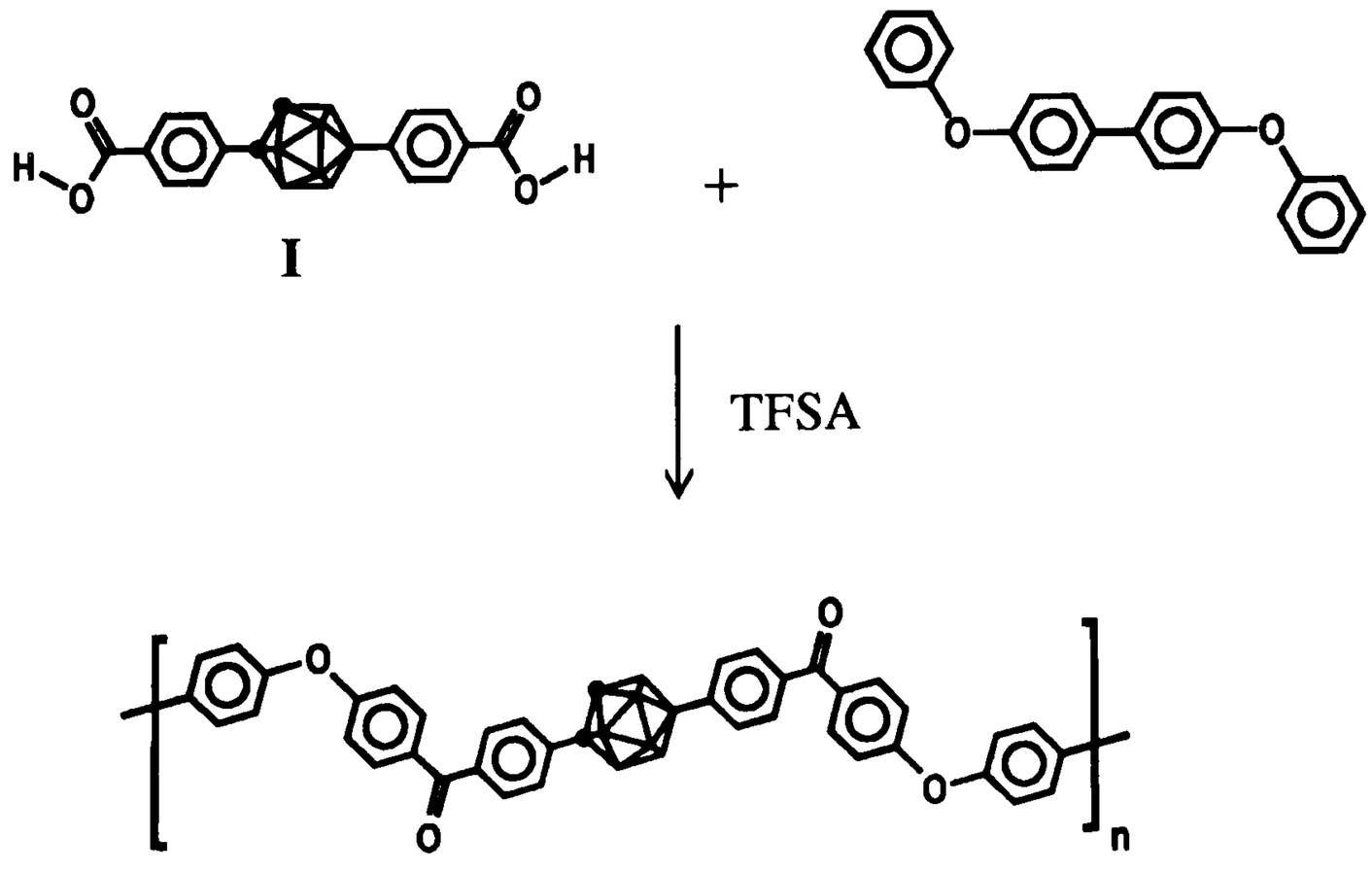
CONCLUSIONS AND FUTURE WORK

From 1,7-bis(4-carboxyphenyl)-*meta*-carborane and 4,4′-diphenoxybiphenyl as monomers, a CPEK has been successfully obtained. The synthesis and model reaction of the novel 1,7-bis(4-phenoxyphenyl)-*meta*-carborane (**XII**) showed that CPEKs could also be produced from this compound.



Possible CPEK formation

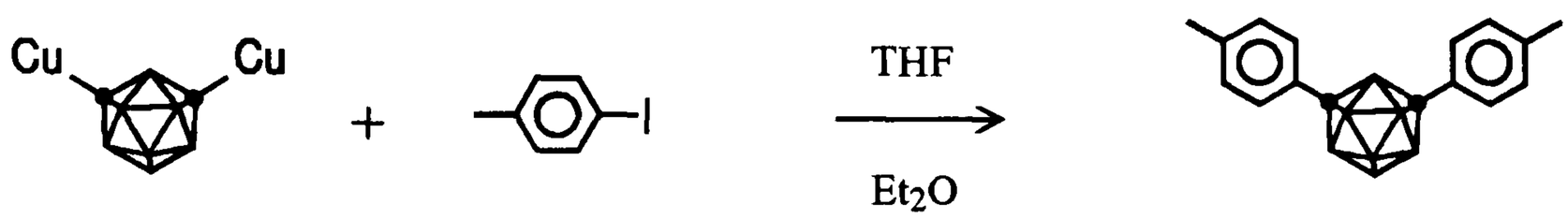
CPEKs could also be formed from 1,12-bis(4-carboxyphenyl)-*ortho*-carborane (**I**) according to the model reaction with anisole in TFSA. The polymer would contain carboranyl carbon-aryl carbon and carboranyl boron-aryl carbon links which may have better thermal properties than CPEKs with just carboranyl carbon-aryl carbon links.



Possible CPEK formation

Compared to the time-consuming synthesis of 1,7-bis(4-methylphenyl)-*meta*-carborane from 6,9-bis(acetonitrile)-decaborane and 4-ethynyltoluene, the formation of the same derivative from the commercially available *meta*-carborane and 4-methylphenyldiazonium tetrafluoroborate is very efficient. Diaryl-*meta*-carboranes formed from this type of reaction could be used for high temperature polymers, ceramics and resins. The scheme overleaf shows potential monomers which could be synthesised from meta carborane.

Recently a similar method using aryl iodides instead of aryldiazonium tetrafluoroborates gave 1,7-diaryl-*meta*-carboranes with improved yields[61].



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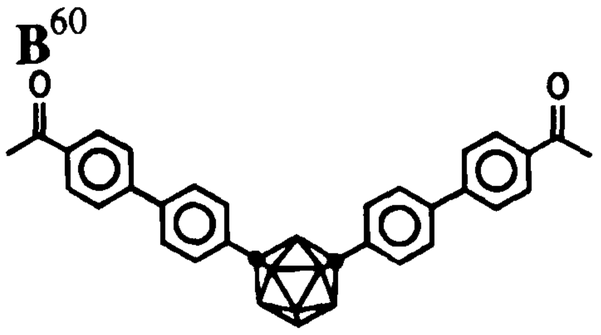
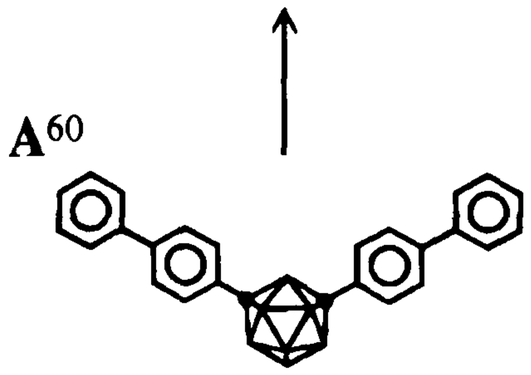
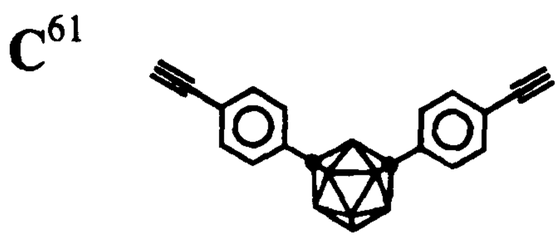


for polyphenylenes (ceramics)





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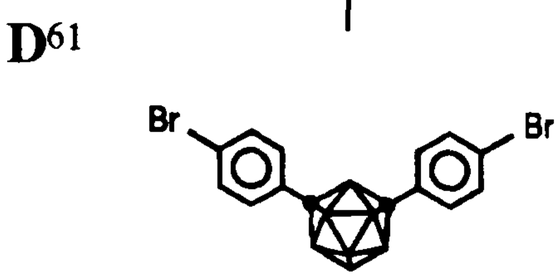

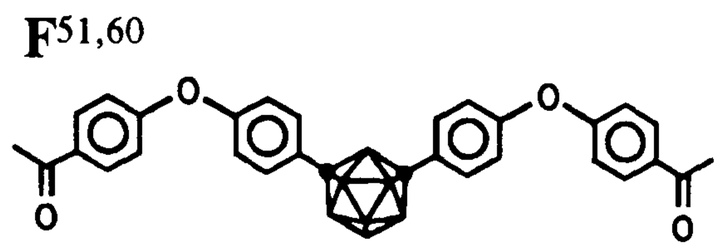

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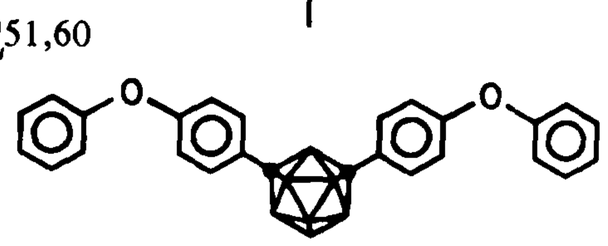

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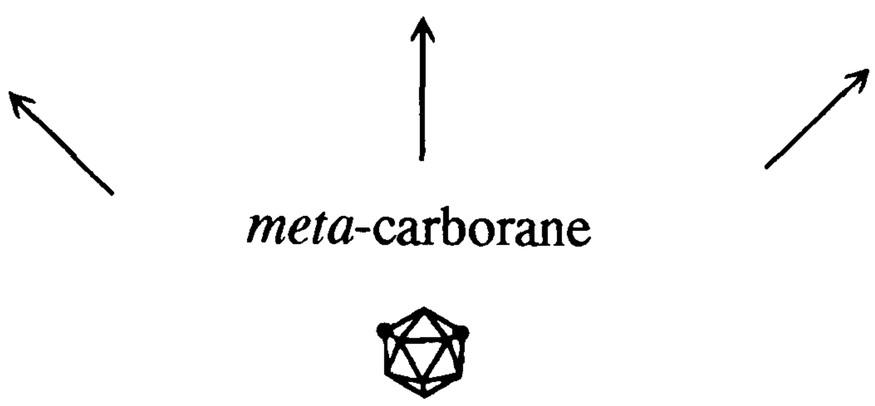
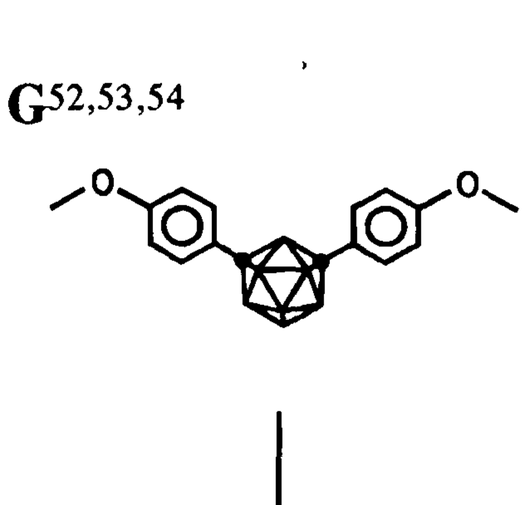
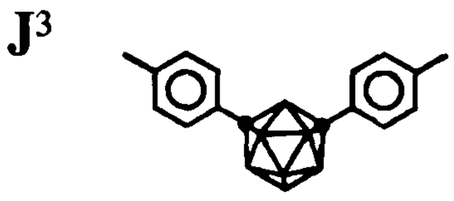
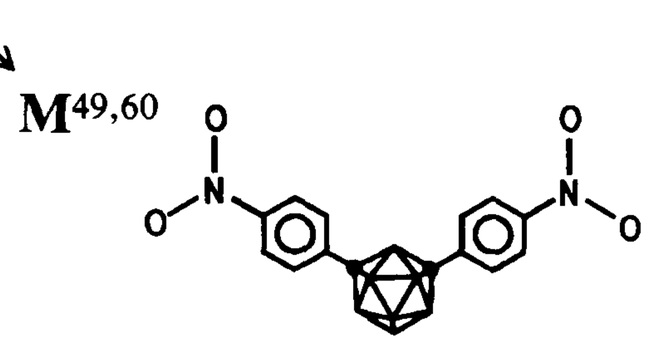
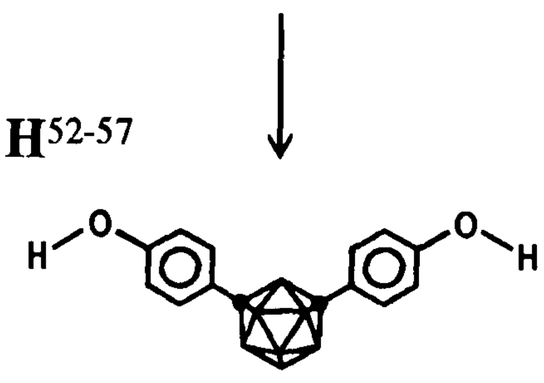


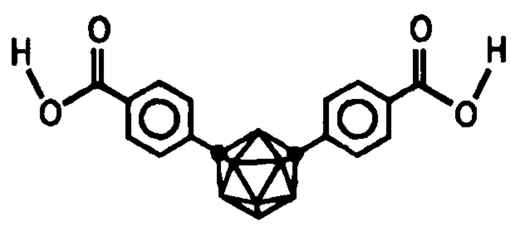




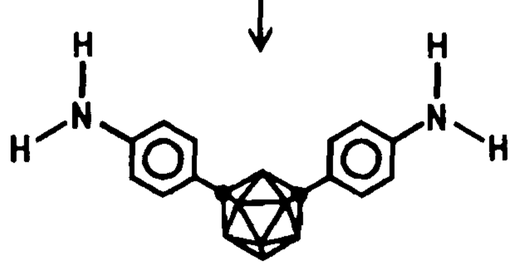




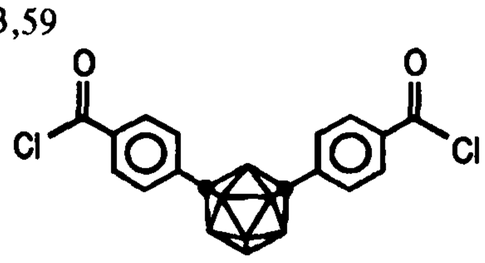
for polyesters and resins



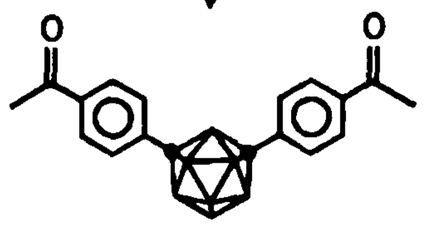
for polyesters, polyamides and polyetherketones



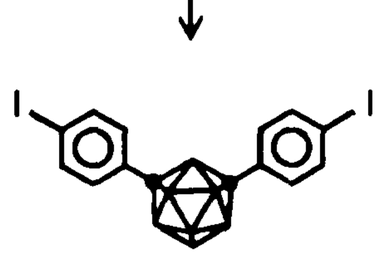
for polyamides



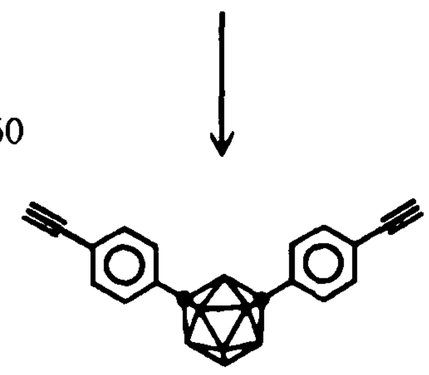
for polyesters and polyamides



for polyphenylenes (ceramics)



for polyethynes (ceramics)



for polyethynes (ceramics)

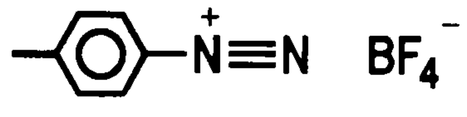
A, B, F, G, H, L, N and O are unknown.

Some references are for ortho carborane analogues.

POSSIBLE FORMATION OF POTENTIAL MONOMERS FROM *META*-CARBORANE

EXPERIMENTAL SECTION

4-methylbenzenediazonium tetrafluoroborate



5.35g (0.05 moles) of *para*-toluidine was dissolved in 24ml of 1:1 hydrochloric acid : water with stirring for 30 minutes at 45°C. At 0°C, over a 15 minute period, 3.65g (0.053 moles) sodium nitrite in 7.5ml water was added slowly to the solution and stirred for 30 minutes. A chilled solution of 7.6g (0.069 moles) sodium tetrafluoroborate in 15ml of water was added dropwise with the temperature still at 0°C and stirred vigorously for 30 minutes. The solid was filtered off, washed with iced water, methanol and diethyl ether, and dried over phosphorus pentoxide to yield 8.3g (80.7%) of 4-methylbenzenediazonium tetrafluoroborate.

Melting point = decomposed at 112-113°C (lit[62]. = decomposed at 114°C)

Analysis Found: C,40.8; H,3.4; N,13.5; F,36.9. $C_7H_7BF_4N_2$ requires C,40.8; H,3.4; N,13.6; F,36.9.

Infrared (Nujol mull; cm^{-1}) 3161(w), 3111(m), 3077(w), 3036(w), 2956(s), 2923(s), 2868(s), 2857(s), 2290(s), 2127(w), 1939(w), 1806(w), 1781(w), 1662(w), 1648(w), 1600(w), 1581(s), 1572(w), 1463(m), 1460(m), 1369(w), 1328(w), 1310(m), 1288(w), 1274(w), 1212(w), 1192(w), 1174(w), 1131(s), 1119(s), 1070(s,br), 1030(s,br), 981(m), 978(w), 823(s), 722(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 110 corresponding to the species $^{12}C_7{}^{1}H_7{}^{19}F$ as a result of decomposition of the salt on heating.

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62. Vogel A.I. "Practical Organic Chemistry" Longmans, Green and Co. London 1948 p611

^{1}H N.M.R. 250.134 MHz; solvent D_2O referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
8.41 8.37 7.76 7.72	4	doublet of doublets	aromatic C-H
2.60	3	singlet	methyl C-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent D_2O, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

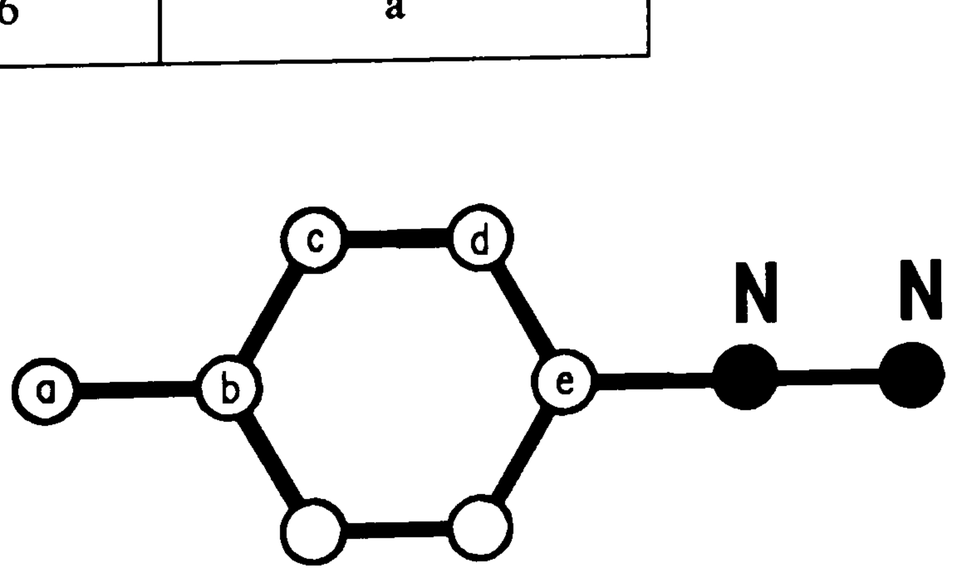
δ_{ppm}	position of boron
-1.40	B-F

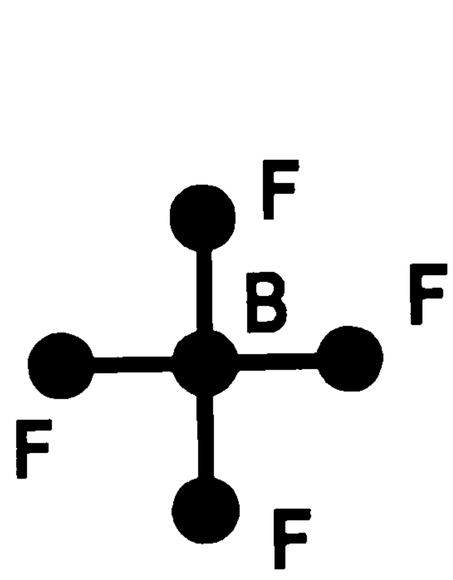
^{19}F N.M.R. {^{1}H broad band noise } 235.342 MHz solvent D_2O, referenced externally to $CFCl_3$ at 0.00ppm.

δ_{ppm}	position of fluorine
-151.34	B-F

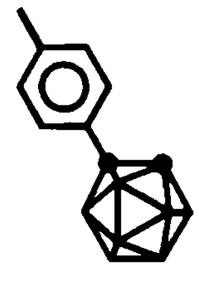
^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent D_2O, referenced externally to $(CH_3)_4Si$ at 0.00ppm.

δ_{ppm}	position of carbon
157.26	b
133.27	c
132.91	d
110.44	e
23.16	a





1-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane



Under nitrogen, a stirred solution of 1.44g (0.01 moles) *ortho*-carborane in 20ml dry diethyl ether was treated dropwise with 17ml (0.01 moles) butyllithium in hexane (0.588M) at 0°C. After 15 minutes, the mixture was boiled for 15 minutes, cooled to 0°C, 1.24g (0.0125 moles) of anhydrous copper (I) chloride was added and then slowly 30ml of dry tetrahydrofuran at 5°C. The solution was stirred at 20°C for 30 minutes and then heated at 40°C for 10 minutes. At 0°C, 2.57g (0.0125 moles) 4-methylbenzenediazonium tetrafluoroborate was added in small portions, with gas evolution, to the solution with vigorous stirring. The mixture was stirred at 0°C for 15 minutes, then 20°C for 15 minutes and finally 40°C for 15 minutes. At 20°C 10ml of methanol was added then the precipitate was filtered off and washed with benzene and diethyl ether. The filtrate was washed with dilute hydrochloric acid, dried over anhydrous magnesium sulphate, filtered and the solvents were pumped off. The residue was dissolved in 20ml absolute alcohol, 10ml glacial acetic acid and 1.5ml concentrated hydrochloric acid and 2g of zinc powder was added in small portions. After boiling the mixture for 2 minutes the zinc powder was filtered off and washed with diethyl ether, the filtrate was diluted with water and extracted with diethyl ether. The ether extracts were washed with water and dried over anhydrous magnesium sulphate, diethyl ether was driven off and the residue was recrystallized from methanol to give 1.47g (62.8%) of 1-(4-methylphenyl)-*ortho*-carborane.

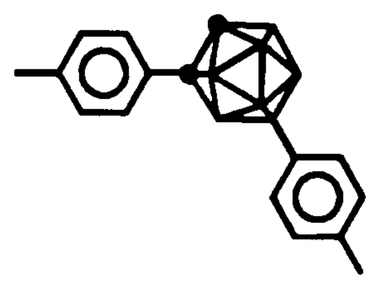
Melting point = 151-153°C (lit. = 155°C)

Attempted formation of 1,9- and 1,12-bis(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane isomers from 9- and 12-iodo-1-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane isomers.

A solution of 8.72g (0.04 moles) 4-iodotoluene in 20ml dry diethyl ether was added dropwise to 1.5g (0.06 moles) of magnesium filings in 20ml anhydrous diethyl ether at 0°C under nitrogen. After reaction, the excess filings were filtered off under nitrogen and the filtrate was added to a solution of 1.80g (5 mmoles) 9- and 12-iodo-1-(4-methylphenyl)-*ortho*-carborane isomers and 0.04g (0.0568 mmoles) of palladium catalyst, $[(C_6H_5)_3P]_2PdCl_2$, in 30ml diethyl ether. The solution was refluxed under nitrogen for 40 hours. After cooling, the black mixture was decomposed with 100ml of distilled water and the organic layer was washed with two 30ml portions each of hydrochloric acid and distilled water, dried over anhydrous magnesium sulphate, filtered and the ether was pumped off. The residue was found to contain unchanged 9- and 12-iodo-1-(4-methylphenyl)-*ortho*-carborane isomers and 4,4′-dimethylbiphenyl by thin layer chromatography and ^{13}C n.m.r. spectroscopy.

1,9- and 1,12-bis(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane isomers

12-isomer

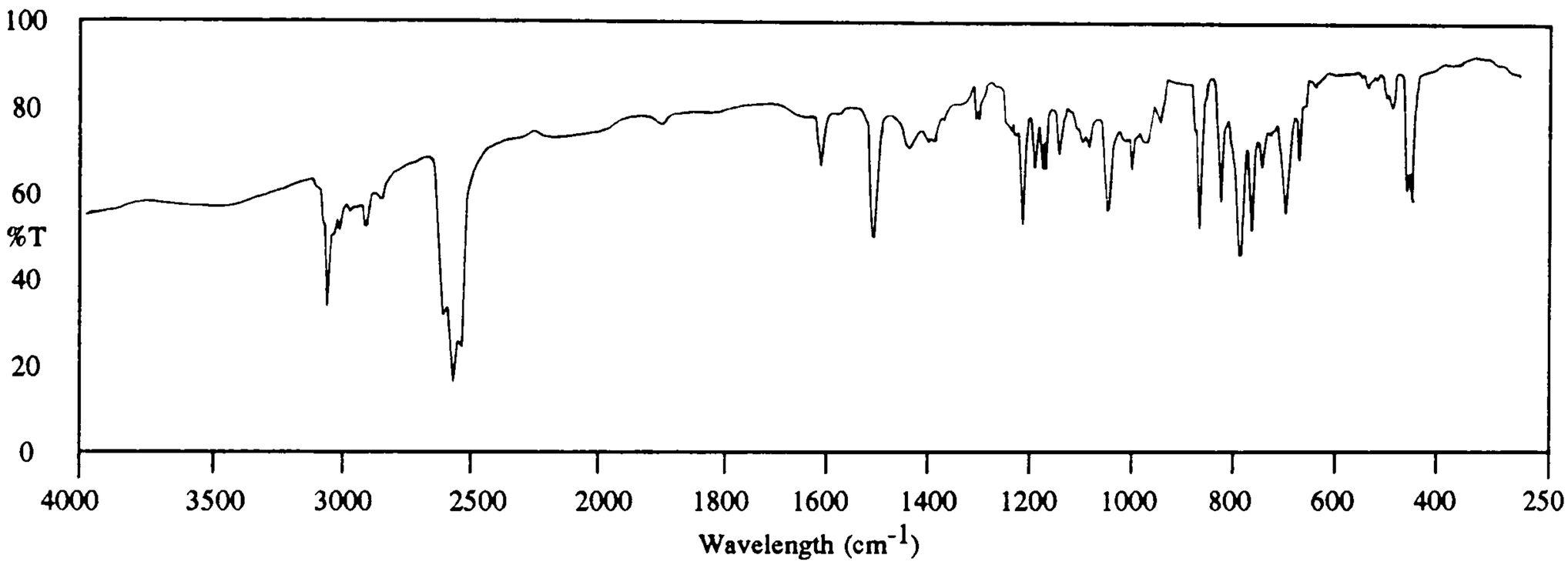


9-isomer

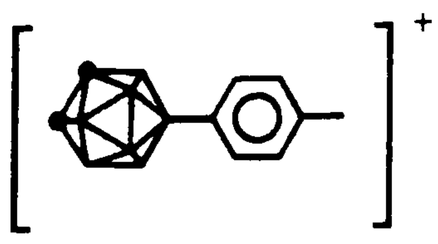
Under nitrogen, a stirred solution of 2.34g (0.01 moles) 9-(4-methylphenyl)-*ortho*-carborane in 20ml dry diethyl ether at 0°C was treated dropwise with 7.1ml (0.01 moles) butyllithium in hexane (1.61M). After 15 minutes, the mixture was boiled for 15 minutes, cooled to 0°C, and 1.24g (0.0125 moles) of anhydrous copper (I) chloride was added followed slowly by 30ml dry tetrahydrofuran at 5°C. The solution was stirred at 20°C for 30 minutes and then heated at 40°C for 10 minutes. At 0°C with vigorous stirring, 2.57g (0.0125 moles) 4-methylbenzenediazonium tetrafluoroborate was added in small portions to the solution with gas evolution and stirred at 0°C for 15 minutes, then 20°C for 15 minutes and finally 40°C for 15 minutes. At 20°C 10ml of methanol was added, the precipitate was filtered off and washed with benzene and diethyl ether. The filtrate was washed with dilute hydrochloric acid, dried over anhydrous magnesium sulphate, filtered and the solvents were removed *in vacuo*. The residue was fractionally sublimed from a bath at 170°C and 0.01mmHg and the fractions containing 1,9- and 1,12-bis(4-methylphenyl)-*ortho*-carborane isomers were combined and recrystallized from hexane. A small amount of pure 1,12-bis(4-methylphenyl)-*ortho*-carborane was obtained by fractional recrystallization. The total yield of 1,9- or 1,12-bis(4-methylphenyl)-*ortho*-carborane crystals was 1.07g (33.0%).

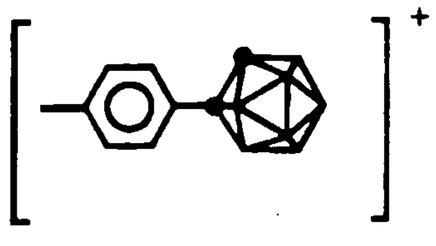
Analysis (of mixture) Found: C,59.4; H,7.7. $C_{16}H_{24}B_{10}$ requires C,59.3; H,7.4.

Infrared (KBr disc; cm^{-1}) 3102(w), 3058(m),3039(w), 3018(w), 2978(w), 2947(w), 2919(w), 2860(w), 2627(m), 2592(s), 2561(s), 1910(w), 1612(w), 1577(w), 1512(m), 1448(w), 1416(w), 1401(w), 1384(w), 1322(w), 1317(w), 1264(w), 1258(w), 1247(w), 1233(m), 1212(w), 1200(w), 1191(w), 1167(w), 1132(w), 1123(w), 1111(w), 1072(m), 1041(w), 1028(w), 1019(w), 1003(w), 974(w), 968(w), 907(w), 899(m), 888(w), 882(w), 859(m), 822(s), 801(m), 791(w), 782(w), 767(w), 737(m), 711(w), 698(w), 681(w), 592(w), 578(w), 545(w), 536(w), 506(m), 497(m), 407(w).



Mass spectrum (C.I.-) A highest mass peak was observed at m/e 326 corresponding to the species $^{12}C_{16}{}^{1}H_{24}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 320 and 326. A group of peaks were seen between m/e 229 and 235 and assigned to either fragment below:





1,12-bis(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

Melting point = 205.5-206.0°C

Analysis Found: C,59.3; H,7.6. $C_{16}H_{24}B_{10}$ requires C,59.3; H,7.4.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

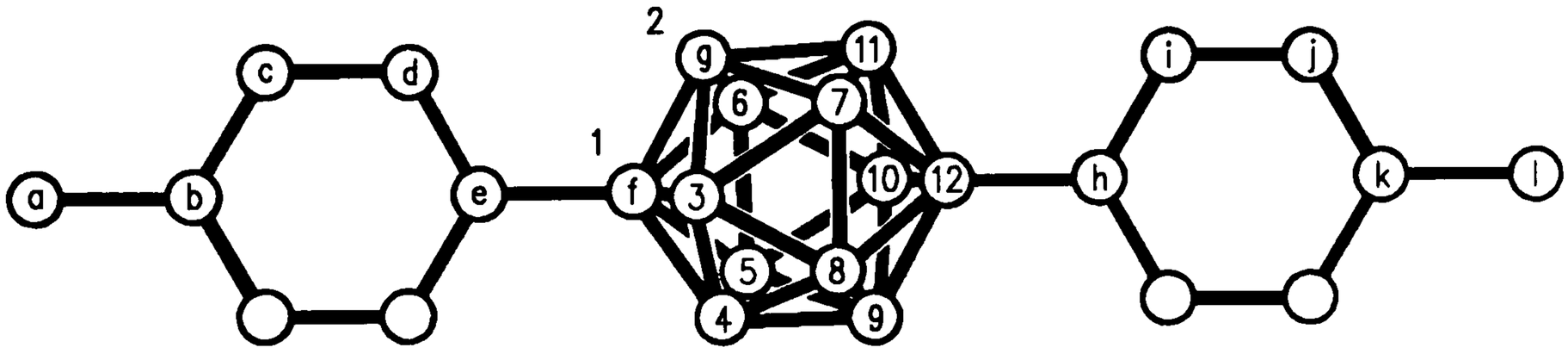
δ_{ppm}	intensity	type of peak	position of proton
7.43 7.40 7.17 7.14	4	doublet of doublets	aromatic C(c,d)-H
7.33 7.30 7.09 7.06	4	doublet of doublets	aromatic C(i,j)-H
4.00	1	broad singlet	carboranyl C(g)-H
2.36	3	singlet	methyl C(a)-H
2.31	3	singlet	methyl C(l)-H
4.0-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
5.96	1	12
-1.54	1	9
-8.14	2	8,10
-11.31	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
140.17	b
136.82	k
132.49	j
130.21	e
129.46	d
128.22	i
127.65	c
70.89	f
59.27	g
21.18	a
20.96	l



1,9-bis(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

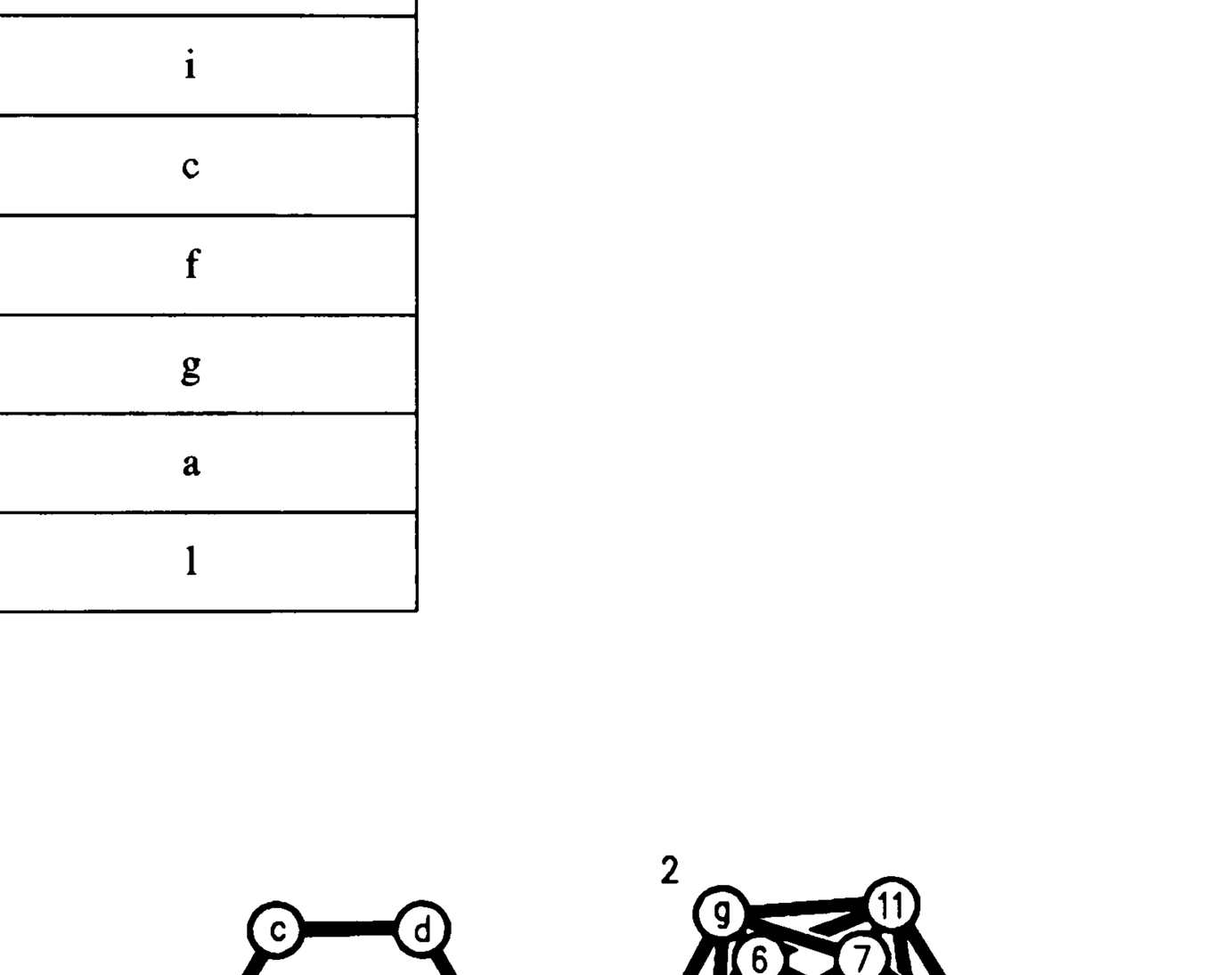
δ_{ppm}	intensity	type of peak	position of proton
7.45 7.42 7.19 7.16	4	doublet of doublets	aromatic C(c,d)-H
7.41 7.38 7.14 7.11	4	doublet of doublets	aromatic C(i,j)-H
3.87	1	broad singlet	carboranyl C(g)-H
2.40	3	singlet	methyl C(a)-H
2.36	3	singlet	methyl C(l)-H
4.0-0.9	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

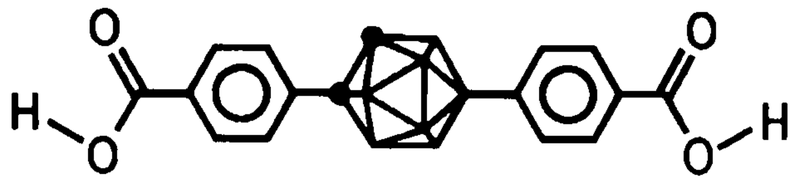
δ_{ppm}	intensity	position of boron
8.14	1	9
-4.16	1	12
-8.14	2	8,10
-11.31	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

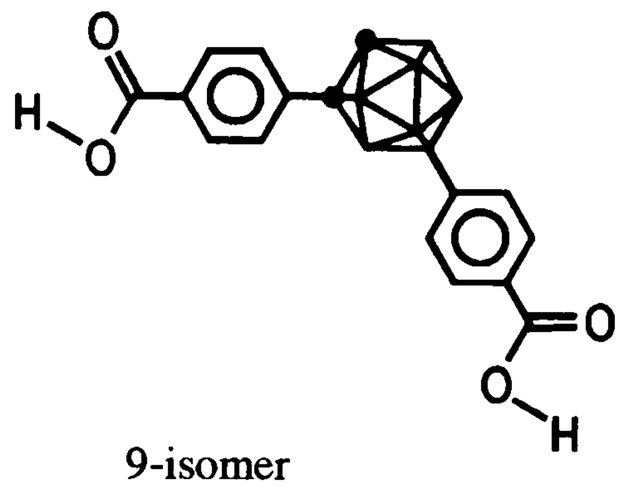
δ_{ppm}	position of carbon
140.17	b
136.78	k
132.36	j
130.58	e
129.46	d
128.23	i
127.48	c
75.35	f
54.72	g
21.16	a
20.93	l



1,9- and 1,12-bis(4-carboxyphenyl)-1,2-dicarba-*closo*-dodecaborane isomers



12-isomer

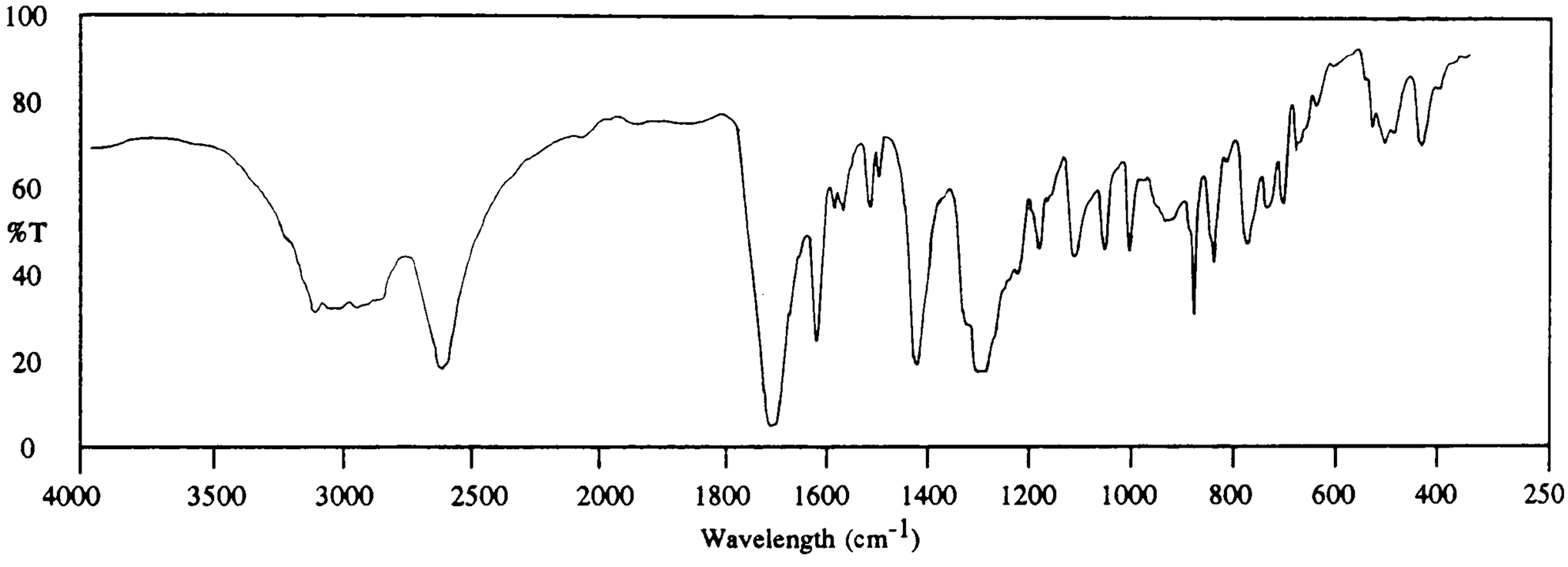


9-isomer

3g (30 mmoles) of chromium trioxide was added in small portions to a stirred mixture of 0.65g (2 mmoles) 1,9- and 1,12-bis(4-methylphenyl)-*ortho*-carborane isomers, 50ml glacial acetic acid, 20ml acetic anhydride and 3ml concentrated sulphuric acid. The dark green mixture was stirred at 20°C for two hours then poured into 300ml distilled water. A precipitate appeared which was filtered off and washed with distilled water to remove the green chromium residues. The off-white solid was dissolved in boiling sodium hydrogen carbonate solution, filtered and then acidified with dilute hydrochloric acid to give a white precipitate. The precipitate was filtered off, recrystallized from a 5:1 acetone : water mixture and dried over phosphorus pentoxide to produce 0.42g (54.5%) of 1,9- and 1,12-bis(4-carboxyphenyl)-*ortho*-carborane isomers.

Analysis Found: C,49.7; H,5.1. $C_{16}H_{20}B_{10}O_4$ requires C,50.0; H,5.2.

Infrared (KBr disc; cm^{-1}) 3420-2100(m,br), 3078(m), 3070(m), 2607(s), 2598(s), 2081(w), 1945(w), 1707(s), 1700(s), 1697(s), 1691(s), 1686(s), 1683(s), 1660(m), 1610(m), 1592(w), 1577(w), 1562(w), 1560(w), 1545(w), 1510(w), 1492(w), 1426(s), 1421(s), 1393(w), 1380(w), 1326(m), 1305(s), 1291(s), 1276(m), 1258(m), 1248(m), 1230(m), 1192(w), 1177(w), 1170(w), 1166(w), 1127(w), 1071(w), 1027(w), 998(w), 972(w), 965(w), 958(w), 949(w), 942(w), 908(w), 902(m), 871(w), 867(w), 842(w), 802(w), 781(w), 763(w), 735(w), 710(w), 704(w), 693(w), 677(w), 672(w), 640(w), 587(w), 571(w), 558(w), 549(w), 532(w), 479(w), 442(w).



Mass spectrum (C.I.-) A highest mass peak was observed at m/e 386 corresponding to the species $^{12}C_{16}{}^{1}H_{20}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 380 and 386.

1,12-bis(4-carboxyphenyl)-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

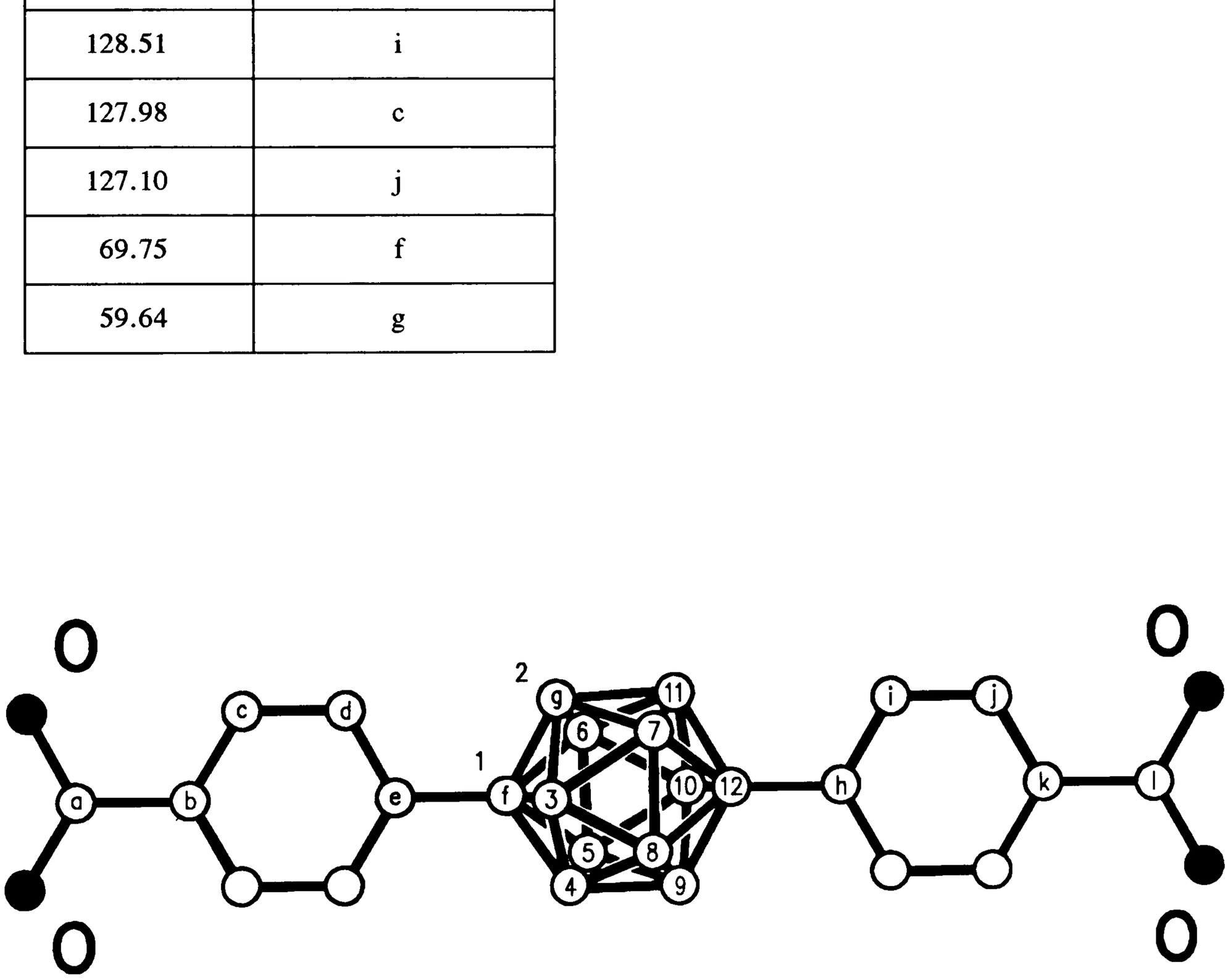
δ_{ppm}	intensity	type of peak	position of proton
8.09 8.05 7.88 7.84	4	doublet of doublets	aromatic C(c,d)-H
7.92 7.89 7.52 7.49	4	doublet of doublets	aromatic C(i,j)-H
7.88	1	singlet	O-H
7.36	1	singlet	O-H
5.50	1	broad singlet	carboranyl C-H
4.0-1.0	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
4.68	1	12
-3.27	1	9
-9.17	2	8,10
-12.07	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$ referenced to 28.0ppm.

δ_{ppm}	position of carbon
164.68	l
161.44	a
133.51	e
131.45	k
131.16	b
128.86	d
128.51	i
127.98	c
127.10	j
69.75	f
59.64	g



1,9-bis(4-carboxyphenyl)-1,2-dicarba-*closo*-dodecaborane

^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

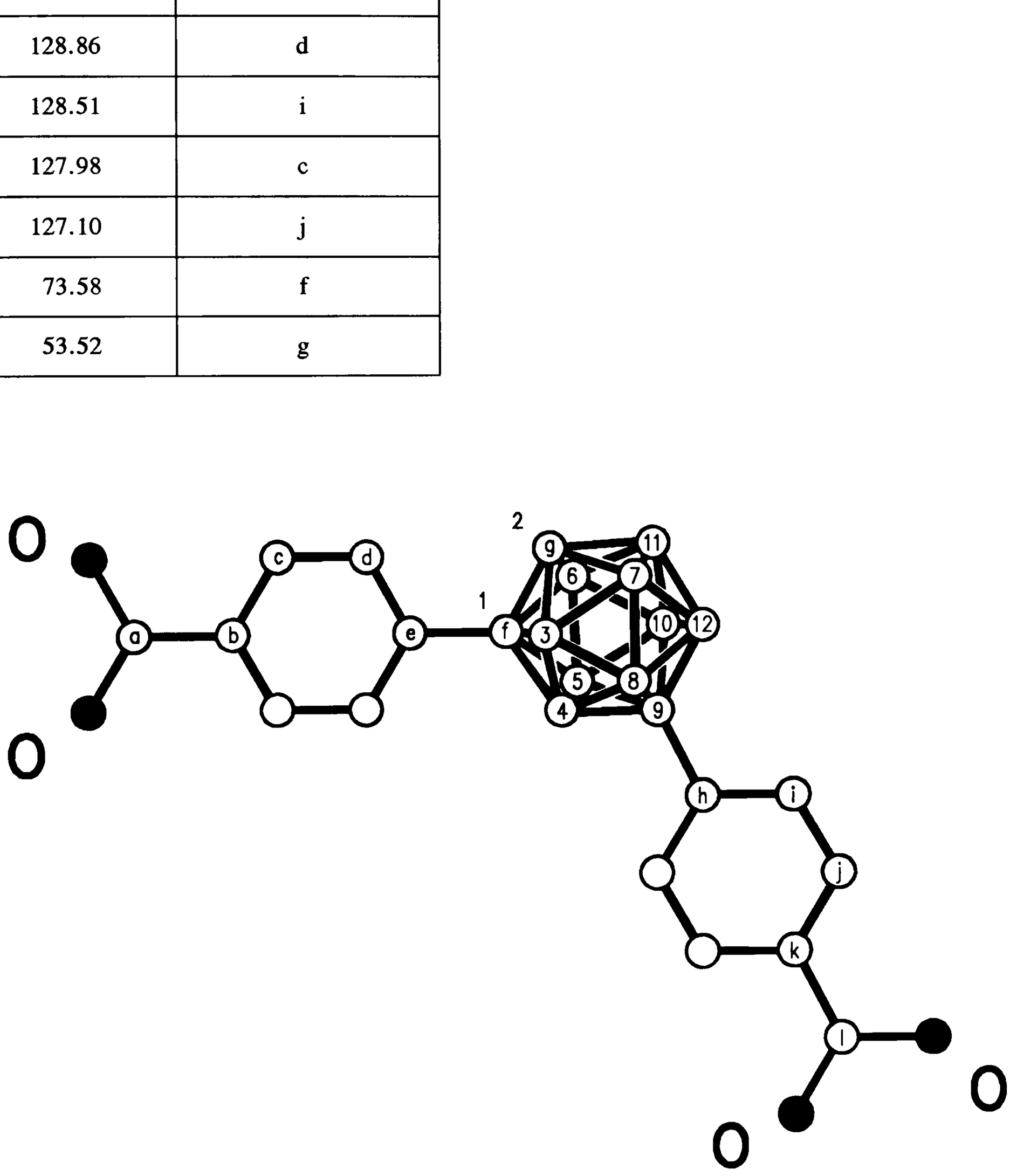
δ_{ppm}	intensity	type of peak	position of proton
8.09 8.05 7.88 7.84	4	doublet of doublets	aromatic C(c,d)-H
7.92 7.89 7.52 7.49	4	doublet of doublets	aromatic C(i,j)-H
7.88	1	singlet	O-H
7.36	1	singlet	O-H
5.50	1	broad singlet	carboranyl C-H
4.0-0.9	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

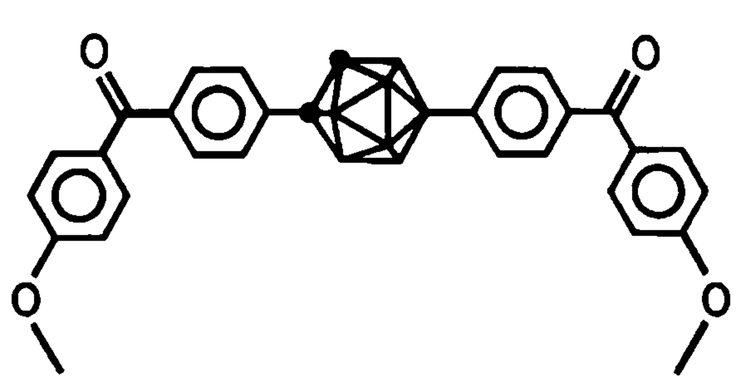
δ_{ppm}	intensity	position of boron
6.88	1	9
-5.46	1	12
-9.17	2	8,10
-12.07	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$ referenced to 28.0ppm.

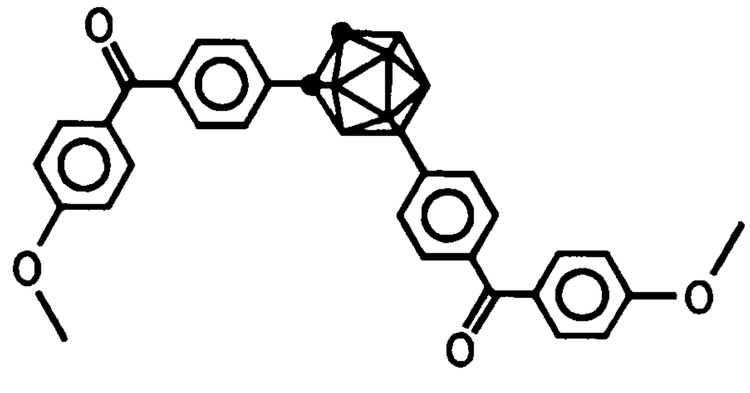
δ_{ppm}	position of carbon
164.68	l
161.44	a
133.98	e
131.45	k
131.16	b
128.86	d
128.51	i
127.98	c
127.10	j
73.58	f
53.52	g



1,9- and 1,12-bis(4′-methoxy-4-benzoylphenyl)-1,2-dicarba-*closo*-dodecaborane isomers



12-isomer

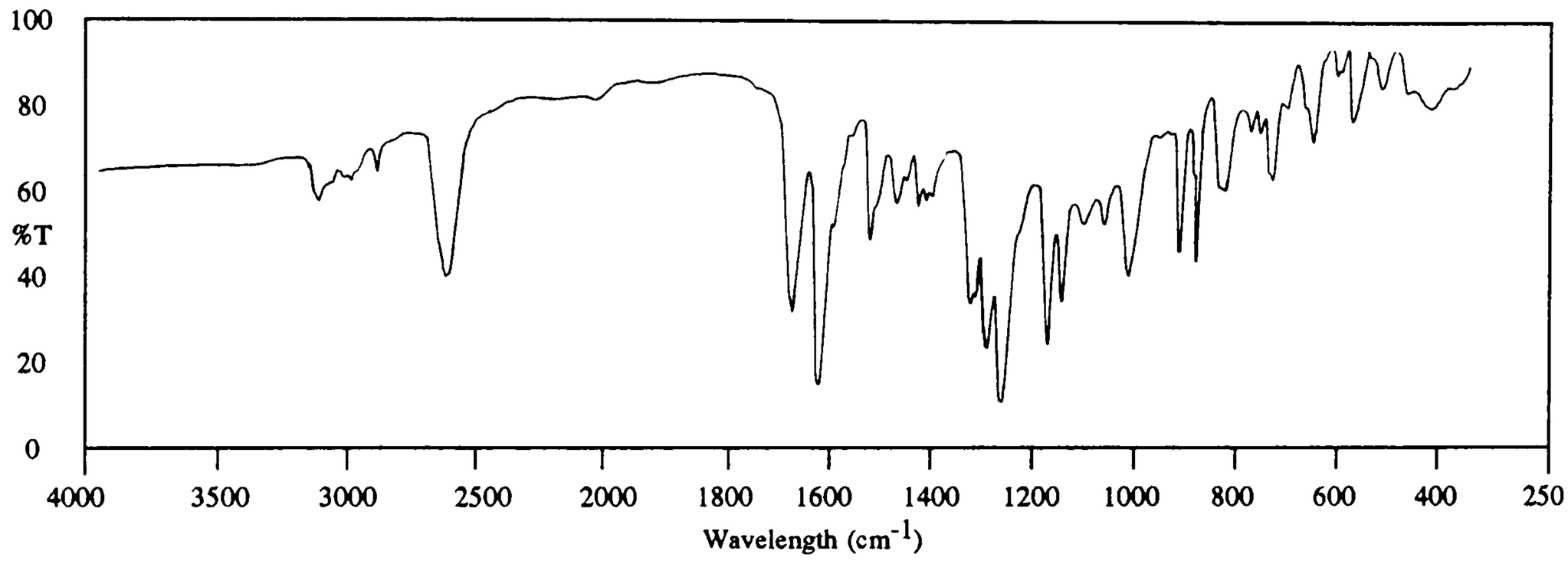


9-isomer

A mixture of 0.192g (0.5 mmoles) 1,9- and 1,12-bis(4-carboxyphenyl)-*ortho*-carborane isomers and 0.12g (1.1 mmoles) anisole was dissolved in 5ml of TFSA and left to stand for 32 hours under nitrogen. The dark red solution was poured into 20ml distilled water affording a white precipitate which was filtered off, washed with distilled water and 10% sodium hydroxide and dried under vacuum. The 0.17g (60.3%) solid was found to be a mixture of 1,9- and 1,12-bis(4′-methoxy-4-benzoylphenyl)-*ortho*-carborane isomers.

Analysis Found: C,58.2; H,5.4. $C_{30}H_{32}B_{10}O_4$ requires C,59.6; H,5.7.

Infrared (KBr disc; cm^{-1}) 3091(w), 3063(m), 3043(w), 3033(w), 3020(w), 2970(w), 2942(w), 2924(w), 2911(w), 2849(w), 2595(m), 2586(m), 2580(m), 1658(m), 1653(m), 1603(s), 1581(w), 1562(w), 1549(w), 1511(m), 1504(w), 1462(w), 1443(w), 1441(w), 1420(w), 1407(w), 1393(w), 1316(m), 1308(m), 1288(s), 1259(s), 1231(w), 1172(m), 1150(m), 1113(w), 1110(w), 1072(w), 1028(m), 930(m), 904(w), 898(m), 858(w), 852(w), 843(w), 798(w), 781(w), 761(w), 757(w), 731(w), 695(w), 681(w), 628(w), 620(w), 608(w), 552(w), 504(w), 455(w), 419(w).



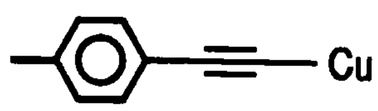
Mass spectrum (C.I.-) A highest mass peak was observed at m/e 564 corresponding to the species $^{12}C_{30}{}^{1}H_{32}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 560 and 566.

Attempted formation of 1,2-bis(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane from 1-(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

Under nitrogen, a stirred solution of 2.34g (0.01 moles) 1-(4-methylphenyl)-*ortho*-carborane in 20ml dry diethyl ether was treated dropwise with 17ml (0.01 moles) butyllithium in hexane (0.588M) at 0°C. After 15 minutes, the mixture was boiled for 15 minutes, cooled to 0°C and 1.24g (0.0125 moles) of anhydrous copper (I) chloride was added followed by 30ml of dry tetrahydrofuran at 5°C. The solution was stirred at 20°C for 30 minutes and then heated at 40°C for 10 minutes. At 0°C, 2.57g (0.0125 moles) 4-methylbenzenediazonium tetrafluoroborate was added in small portions to the solution with vigorous stirring but little gas evolution occured. The mixture was stirred at 0°C for 15 minutes, then 20°C for 15 minutes and finally 40°C for 15 minutes. At 20°C 10ml of methanol was added to the mixture then the precipitate was filtered off and washed with benzene and diethyl ether. The filtrate was washed with dilute hydrochloric acid, dried over anhydrous magnesium sulphate, filtered and the solvents were removed *in vacuo* to leave a green solid.

The residue was dissolved in 20ml absolute alcohol, 10ml glacial acetic acid and 1.5ml concentrated hydrochloric acid and 2g of zinc powder was added in small portions. After the mixture had been boiled for 2 minutes, the excess zinc powder was filtered off and washed with diethyl ether. The colourless filtrate was diluted with water and extracted with diethyl ether. The ether extracts were combined, washed with water, dried over anhydrous magnesium sulphate and filtered. Ether was driven off and the residue was found to contain only unchanged 1-(4-methylphenyl)-*ortho*-carborane by infrared spectroscopy and thin layer chromatography on silica with a 1:1 hexane : toluene mixture as eluent.

4-methylphenylethynyl copper

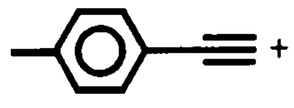


19.05g (0.1 moles) of copper (I) iodide dissolved in 150ml concentrated aqueous ammonia solution (0.88M) was added dropwise to a solution of 11.6g (0.1 moles) 4-ethynyltoluene in 500ml alcohol with a mechanical stirrer. A yellow precipitate was produced and after addition the slurry was stirred for an hour then the precipitate was filtered off, washed thoroughly with water, ethanol and diethyl ether. The bright yellow solid was dried *in vacuo* for two hours to produce 11.4g (63.9%) of 4-methylphenylethynyl copper.

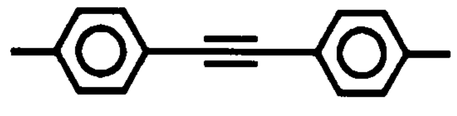
Analysis Found: C,63.6; H,4.1. C_9H_7Cu requires C,60.5; H,3.9.

Infrared (KBr disc; cm^{-1}) 3077(w), 3021(w), 2970(w), 2917(w), 2855(w), 1937(w), 1895(w), 1645(w), 1608(w), 1566(w), 1504(s), 1448(w), 1409(w), 1377(w), 1309(w), 1264(w), 1232(w), 1212(w), 1195(w), 1178(w), 1118(w), 1101(w), 1037(w), 1023(w), 957(w), 936(w), 829(w), 808(s), 703(w), 647(w), 526(m), 520(m), 491(w), 457(w), 419(w), 408(w), 384(w), 353(w), 345(w), 312(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 230 corresponding to the species $^{12}C_{18}{}^{1}H_{14}$ which is probably 1,4-bis(4-methylphenyl)butadiyne formed by $^{12}C_9{}^{1}H_7$ fragments. A peak of m/e 115 appeared, corresponding to:



Bis(4-methylphenyl)acetylene



METHOD A

10.9g of 4-iodotoluene was dissolved in 100ml of diethylamine and acetylene was slowly bubbled through the solution via a gas inlet. After one hour, the solution was treated with a catalytic mixture of 0.02g (1.04 mmoles) anhydrous copper (I) iodide and 0.07g (0.0886 mmoles) bis(triphenylphosphino)palladium dichloride. The acetylene was left to flow through the solution for 4 hours where a dark brown liquid appeared. Diethylamine was removed from the mixture under vacuum and the dark oily residue was dissolved in methanol, decolorized with activated charcoal and filtered. The methanol filtrate gave 1.40g (27.2%) crystals of bis(4-methylphenyl)acetylene and a brown oil was present after the methanol was evaporated. The oil, which is probably crude 4-ethynyltoluene (by infrared spectroscopy), was not purified.

METHOD B

A solution of 10.9g (0.05 moles) 4-iodotoluene in 40ml dry pyridine was added to a stirred suspension of 8.93g (0.05 moles) 4-methylphenylethynyl copper in 140ml anhydrous pyridine under nitrogen. The mixture was refluxed for 18 hours under nitrogen producing a dark brown solution. After cooling, it was poured into 500ml distilled water and the organic products extracted by three 30ml portions of diethyl ether. The combined ether extracts were washed thoroughly with two molar hydrochloric acid, aqueous sodium hydrogen carbonate and finally water. The light brown ether solution was dried over anhydrous magnesium sulphate,

filtered and the ether removed by rotary evaporator to leave a solid. The residue was dissolved in hot methanol and decolorized with activated charcoal. After the charcoal had been removed by filtration, the solution afforded 7.6g (73.8%) of off-white crystals identified as bis-(4-methylphenyl)acetylene.

Melting point = 133-134°C (lit[63]. = 136°C)

Analysis Found: C,93.2; H,6.9. $C_{16}H_{14}$ requires C,93.2; H,6.8.

Infrared (KBr disc; cm^{-1}) 3082(w), 3063(w), 3040(w), 3033(w), 2959(w), 2926(m), 2862(w), 2139(w), 1913(w), 1658(w), 1607(w), 1543(w), 1519(m), 1507(m), 1461(w), 1448(w), 1412(w), 1379(w), 1312(w), 1262(w), 1211(w), 1185(w), 1176(w), 1123(w), 1108(w), 1100(w), 1037(w), 1020(w), 962(w), 947(w), 857(w), 840(m), 816(s), 708(w), 602(w), 516(w), 509(m), 465(w), 408(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 206 corresponding to the species $^{12}C_{16}{}^{1}H_{14}$. Another peak was present at m/e 191 identified as:

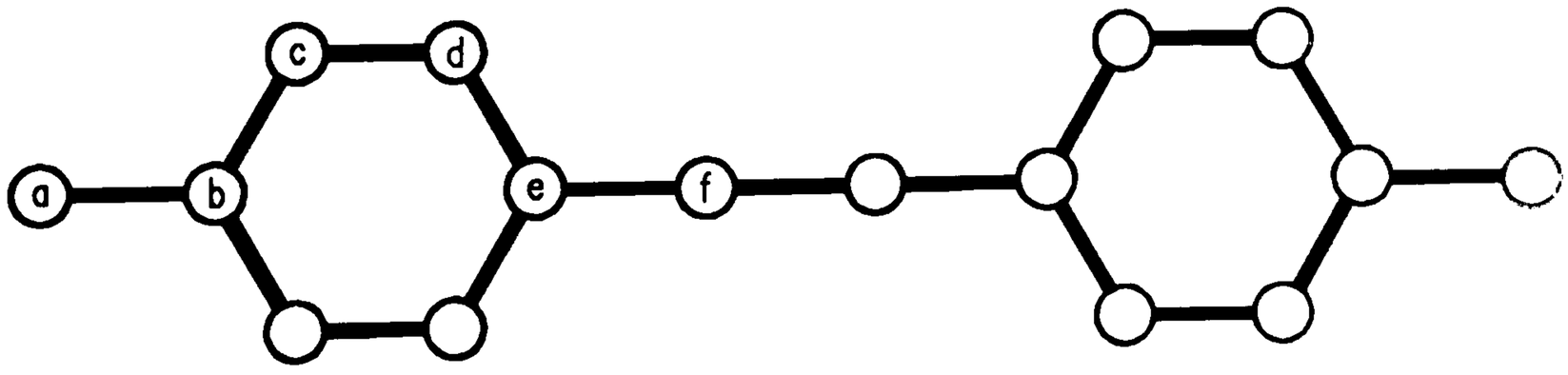
63. Drefahl G. Plotner G. *Chem. Ber.* 1958 **91** 1280-1285

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

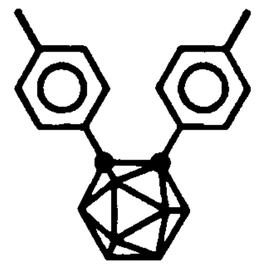
δ_{ppm}	intensity	type of peak	position of proton
7.44 7.41 7.17 7.14	8	doublet of doublets	aromatic C-H
2.37	6	singlet	methyl C-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
138.13	b
131.42	d
129.05	c
120.44	e
88.88	f
21.44	a



1,2-bis(4-methylphenyl)-1,2-dicarba-*closo*-dodecaborane

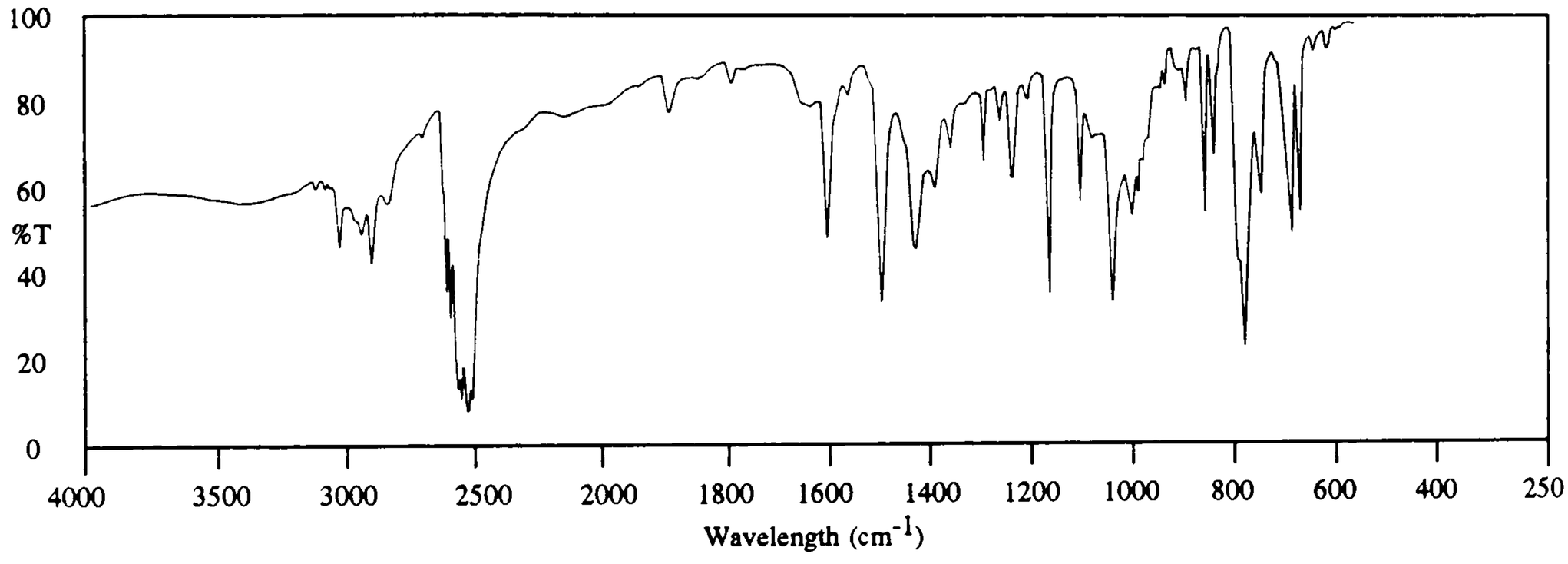


A solution of 7.21g (0.035 moles) bis(4-methylphenyl)acetylene dissolved in 60ml dry toluene was added to a stirred slurry of 7.07g (0.035 moles) 6,9-bis(acetonitrile)-decaborane in 60ml anhydrous toluene under nitrogen. The mixture was heated cautiously, giving gas evolution, and then refluxed for 24 hours. The red solution was cooled, mixed with 40ml methanol and stirred until no further hydrogen was evolved. The solvents were removed by rotary evaporator and *in vacuo* leaving a brown solid which was ground to a powder and refluxed with hexane. The solution was filtered and the hexane was removed by a rotary evaporator to leave a yellow solid. The residue was recrystallized from hexane to give 5.2g (45.9%) of 1,2-bis(4-methylphenyl)-*ortho*-carborane.

Melting point = 170-172°C (lit[3]. = 171-172°C)

Analysis Found: C,59.8; H,7.5. $C_{16}H_{24}B_{10}$ requires C,59.3; H,7.4.

Infrared (KBr disc; cm^{-1}) 3122(w), 3088(w), 3072(w), 3031(w), 2972(w), 2953(w), 2916(w), 2860(w), 2748(w), 2655(w), 2647(m), 2632(m), 2608(s), 2600(s), 2588(s), 2563(s), 2549(s), 1907(w), 1787(w), 1642(w), 1611(m), 1571(w), 1510(m), 1443(m), 1408(w), 1376(w), 1349(w), 1313(w), 1298(w), 1282(w), 1260(w), 1229(w), 1191(m), 1131(w), 1109(w), 1096(w), 1072(m), 1034(m), 1022(w), 1012(w), 1003(w), 978(w), 968(w), 942(w), 928(w), 907(w), 895(m), 877(w), 832(m), 824(s), 817(m), 788(w), 737(w), 729(m), 712(m), 682(w), 656(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 326 corresponding to the species $^{12}C_{16}{}^{1}H_{24}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 320 and 326.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

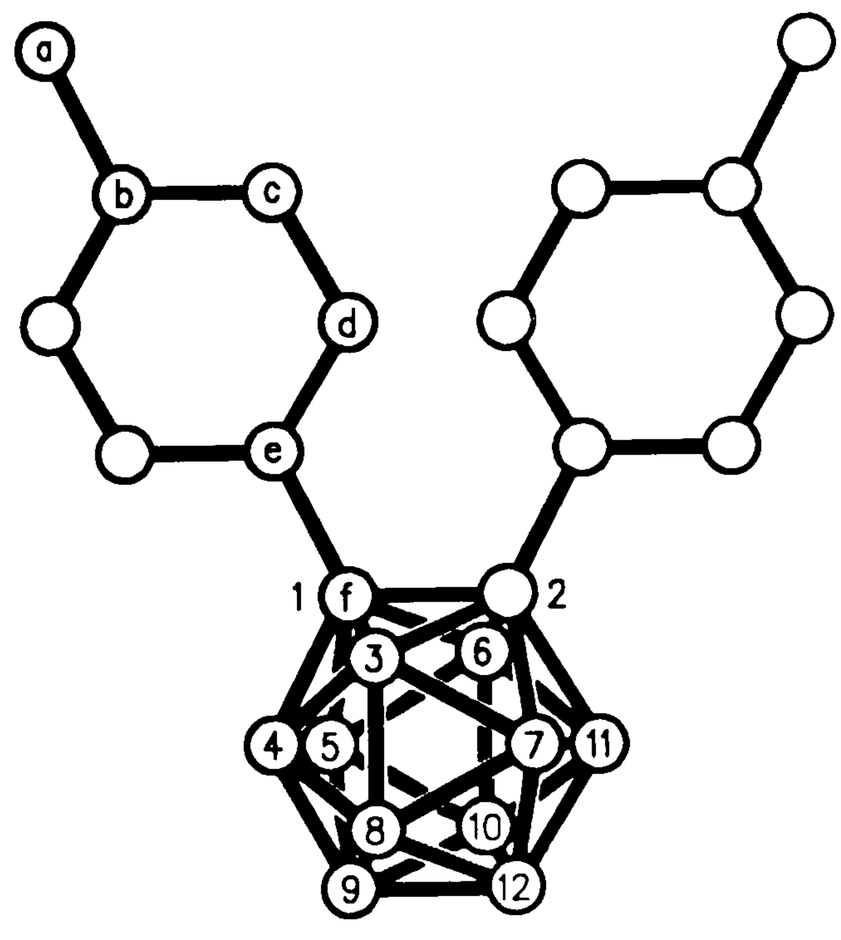
δ_{ppm}	intensity	type of peak	position of proton
7.31 7.28 6.94 6.91	8	doublet of doublets	aromatic C(c,d)-H
2.20	6	singlet	methyl C(a)-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

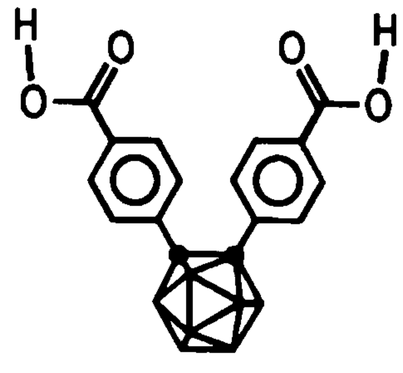
δ_{ppm}	intensity	position of boron
-2.52	2	9,12
-9.03	4	4,5,7,11
-10.42	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
140.29	b
130.46	d
128.90	c
127.99	e
85.47	f
20.95	a



1,2-bis(4-carboxyphenyl)-1,2-dicarba-*closo*-dodecaborane

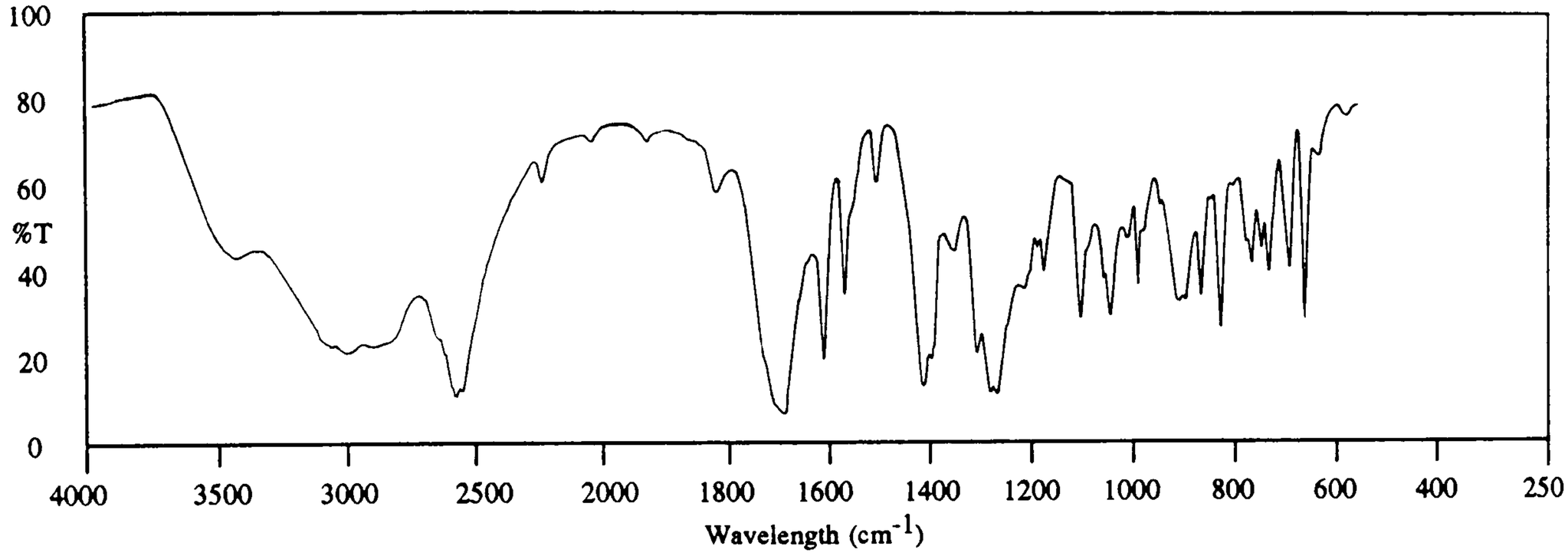


3g (30 mmoles) of chromium trioxide was added in small portions to a stirred mixture of 0.65g (2 mmoles) 1,2-bis(4-methylphenyl)-*ortho*-carborane, 50ml glacial acetic acid, 20ml acetic anhydride and 3ml concentrated sulphuric acid. The dark green mixture was stirred at 20°C for two hours then poured into a beaker of 300ml distilled water. A precipitate slowly appeared which was filtered off and washed well with distilled water to remove the green chromium residues. The off-white solid was dissolved in boiling sodium hydrogen carbonate solution and left to cool giving a clear crystalline solid. The solid was filtered off, dissolved in distilled water and then acidified with dilute hydrochloric acid affording a white precipitate. The precipitate was filtered off and recrystallized from an acetone : water mixture to produce 0.47g (61.2%) of 1,2-bis(4-carboxyphenyl)-*ortho*-carborane.

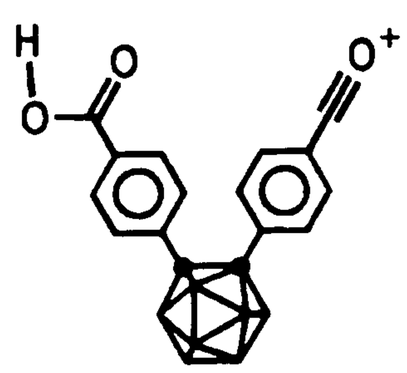
Melting point = over 320°C (lit[3]. = decomposed at 350°C)

Analysis Found: C,50.2; H,5.4. $C_{16}H_{20}B_{10}O_4$ requires C,50.0; H,5.3.

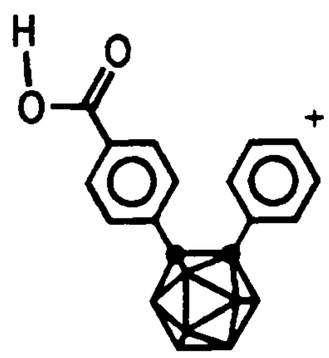
Infrared (KBr disc; cm^{-1}) 3680-2210(m,br), 2662(m), 2636(m), 2598(s), 2575(s), 2269(w), 2087(w), 1939(w), 1808(w), 1705(s), 1690(s), 1612(m), 1571(m), 1563(w), 1508(w), 1423(s), 1408(m), 1375(w), 1322(m), 1298(s), 1287(s), 1265(m), 1232(m), 1205(w), 1193(w), 1127(m), 1082(w), 1071(m), 1038(w), 1019(w), 1008(w), 978(w), 943(m), 931(m), 900(m), 879(w), 862(m), 839(w), 812(w), 803(w), 783(w), 771(w), 731(w), 701(m), 677(w).



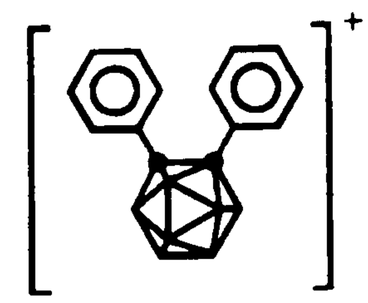
Mass spectrum (E.I.) A highest mass peak was observed at m/e 386 corresponding to the species $^{12}C_{16}{}^{1}H_{20}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 380 and 386. Three other groups of peaks were seen and identified as:



m/e 363-369



m/e 335-341



m/e 290-296

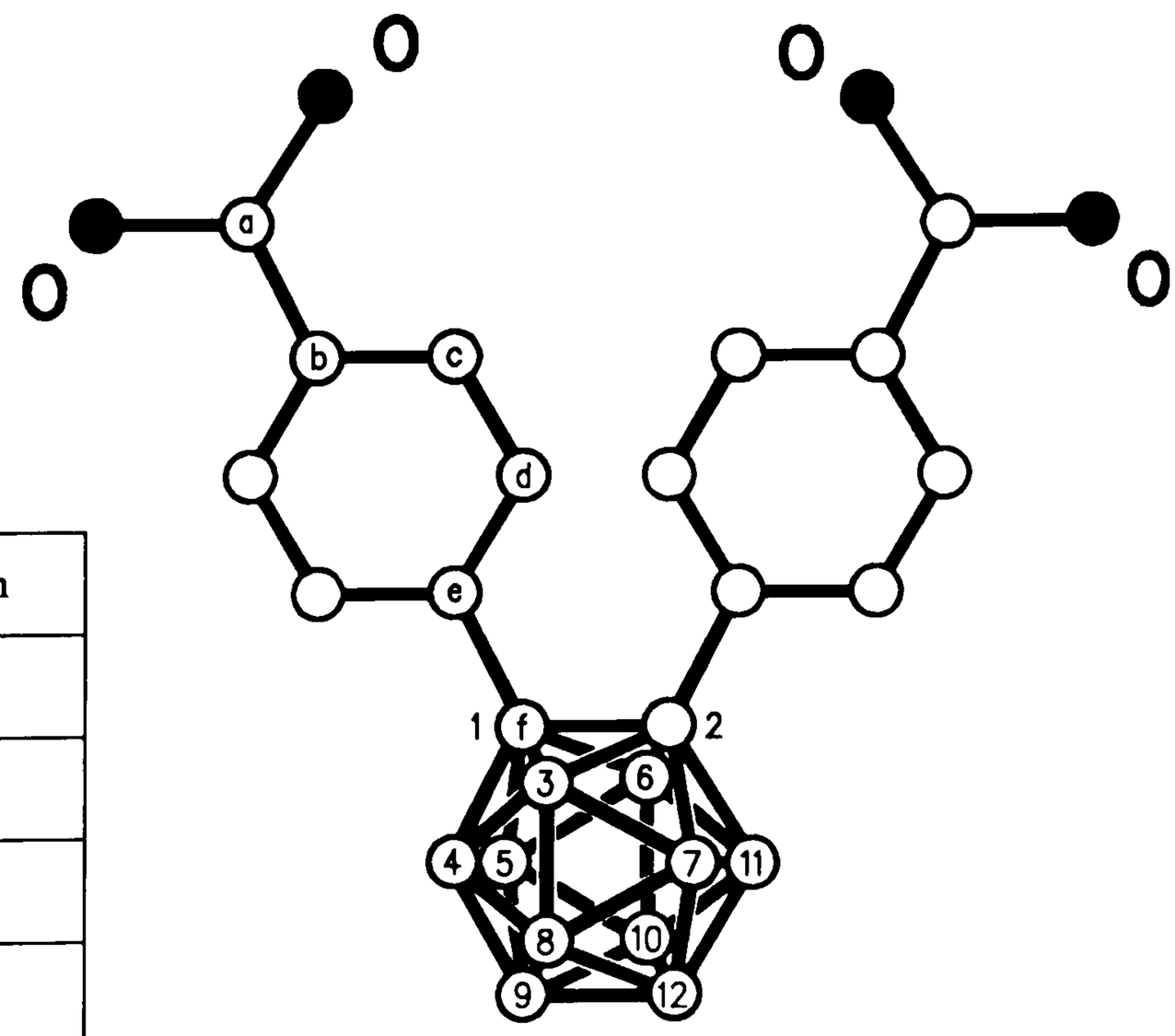
^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

δ_{ppm}	intensity	type of peak	position of proton
8.16	2	broad singlet	O-H
7.89 7.86 7.77 7.74	8	doublet of doublets	aromatic C-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

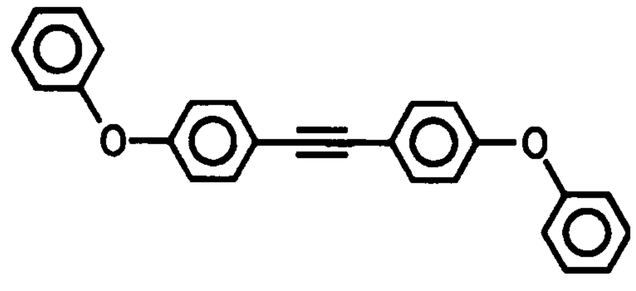
δ_{ppm}	intensity	position of boron
-1.35	2	9,12
-9.23	8	3,6,4,5,7,11,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$ referenced to 28.0ppm.



δ_{ppm}	position of carbon
164.45	a
133.15	e
131.51	b
130.15	d
128.69	c
83.67	f

Bis(4-phenoxyphenyl)acetylene



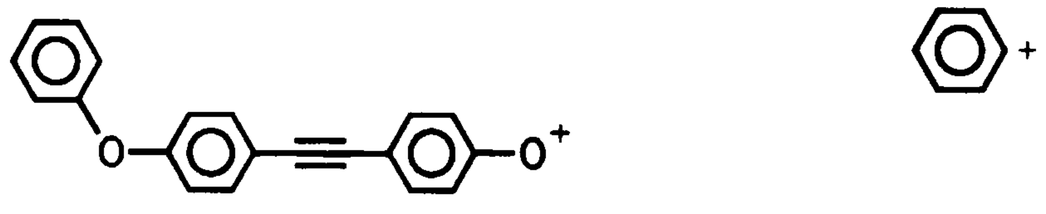
16.2g (0.055 moles) 4-iododiphenyl ether was dissolved in 80ml diethylamine with stirring under nitrogen. A stream of acetylene (purified by passage through a concentrated sulphuric acid trap to remove acetone) was passed through the amine solution. After ten minutes a catalytic mixture of 0.07g (0.0886 mmoles) $(Ph_3P)_2PdCl_2$ and 0.02g (1.04 mmoles) anhydrous copper (I) iodide was added to the stirred solution with a rate of approximately one bubble every 15 seconds of acetylene. After an hour a white solid appeared and after 12 hours acetylene was stopped. The solid was filtered off and washed well with methanol to give 7.2g (72.3%) of bis(4-phenoxyphenyl)acetylene.

Melting point = 169-170°C (lit[51]. = 171°C)

Analysis Found: C,85.9; H,5.1. $C_{26}H_{18}O_2$ requires C,86.2; H,4.9.

Infrared (KBr disc; cm^{-1}) 3095(w), 3076(w), 3063(w), 3047(w), 1910(w), 1731(w), 1671(w), 1596(s), 1592(s), 1974(w), 1515(s), 1492(s), 1474(m), 1455(w), 1412(w), 1336(w), 1318(w), 1310(w), 1303(w), 1278(s), 1256(s), 1198(m), 1167(s), 1153(w), 1150(w), 1106(m), 1072(m), 1022(w), 1013(w), 1003(w), 962(w), 958(w), 899(w), 877(m), 850(s), 838(s), 827(m), 820(w), 775(m), 739(s), 717(w), 692(s), 614(w), 527(w), 517(m), 483(m), 464(w), 407(w), 399(w), 390(w).

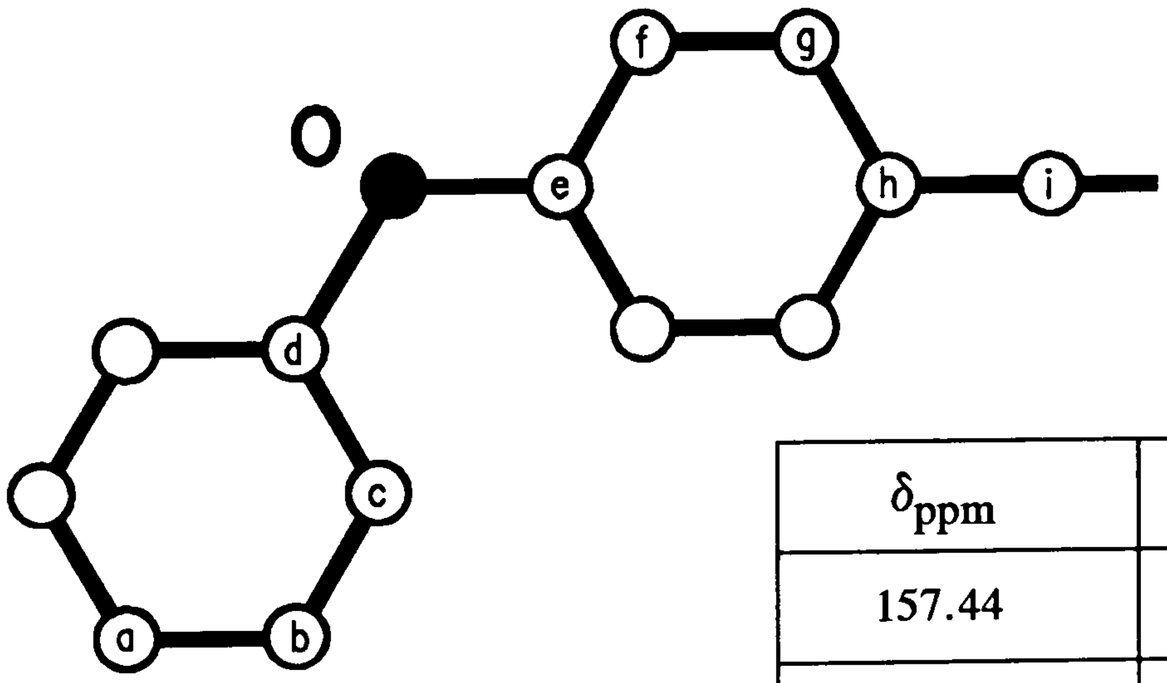
Mass spectrum (E.I.) A highest mass peak was observed at m/e 362 corresponding to the species $^{12}C_{26}{}^{1}H_{18}{}^{16}O_2$. Two peaks were also present at m/e 285 and m/e 77 were assigned respectively to:



^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

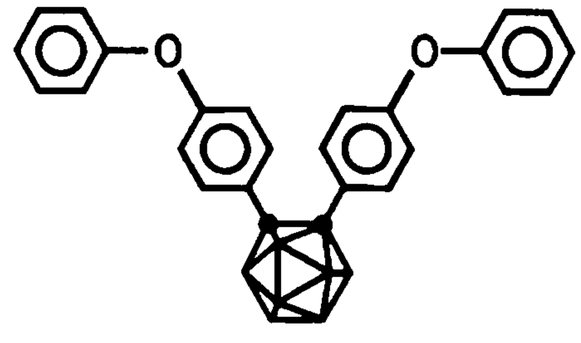
δ_{ppm}	intensity	type of peak	position of proton
7.38 7.35 7.07 7.04	8	doublet of doublets	aromatic C(f,g)-H
7.51-6.96	10	multiplet	aromatic C(a,b,c)-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.



δ_{ppm}	position of carbon
157.44	d
156.44	e
133.03	b
129.80	g
123.74	a
119.33	f
118.35	c
117.91	h
88.27	i

1,2-bis(4-phenoxyphenyl)-1,2-dicarba-*closo*-dodecaborane

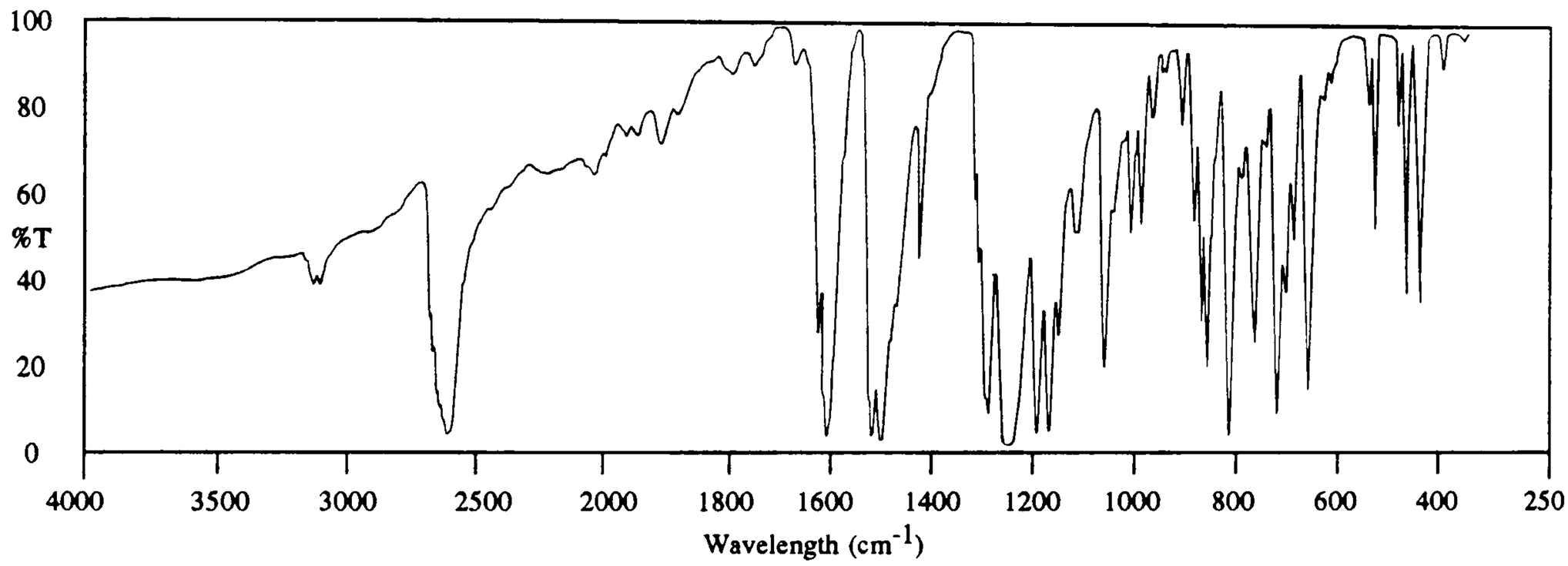


A solution of 5.43g (0.015 moles) bis(4-phenoxyphenyl)acetylene dissolved in 60ml dry toluene was added to a stirred slurry of 3.03g (0.015 moles) 6,9-bis(acetonitrile)-decaborane in 60ml anhydrous toluene under nitrogen. The mixture was heated cautiously, giving gas evolution, and then refluxed for 24 hours. The red solution was cooled, mixed with 40ml methanol and stirred until no further hydrogen gas was evolved. The solvents were removed by rotary evaporator and *in vacuo* to leave a brown solid which was ground to a powder and refluxed with hexane. The solution was filtered and the hexane was vacuum-removed to give an off-white solid which was recrystallized from absolute alcohol to yield 2.60g (53.5%) of 1,2-bis(4-phenoxyphenyl)-*ortho*-carborane crystals.

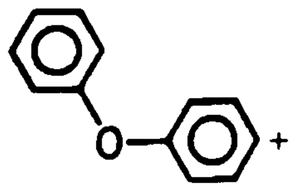
Melting point = 118-120°C (lit[51]. = 120-122°C)

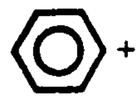
Analysis Found: C,65.1; H,5.4. $C_{26}H_{28}B_{10}O_2$ requires C,65.0; H,5.4.

Infrared (KBr disc; cm^{-1}) 3105(w), 3080(w), 3056(w), 2647(m), 2638(m), 2620(s), 2608(s), 2597(s), 2580(s), 2566(s), 2045(w), 1966(w), 1946(w), 1902(w), 1872(w), 1781(w), 1773(w), 1732(w), 1722(w), 1658(w), 1654(w), 1609(m), 1597(s), 1591(s), 1507(s), 1489(s), 1473(m), 1461(m), 1419(m), 1397(w), 1315(w), 1308(m), 1289(s), 1269(s), 1250(s), 1244(s), 1199(s), 1178(s), 1161(m), 1128(w), 1123(w), 1073(m), 1058(w), 1037(w), 1023(w), 1015(w), 1005(w), 983(w), 963(w), 959(w), 943(w), 927(w), 906(w), 892(m), 882(m), 876(w), 867(w), 840(s), 828(w), 824(w), 790(m), 770(w), 750(s), 732(m), 717(w), 690(s), 658(w), 644(w), 639(w), 572(w), 561(w), 517(w), 501(m), 474(m), 430(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 482 corresponding to the species $^{12}C_{26}{}^{1}H_{28}{}^{11}B_{10}{}^{16}O_2$, accompanied by the usual carborane isotope distribution pattern between m/e 476 and 482. Peaks observed at m/e 169 and m/e 77 were assigned respectively to:





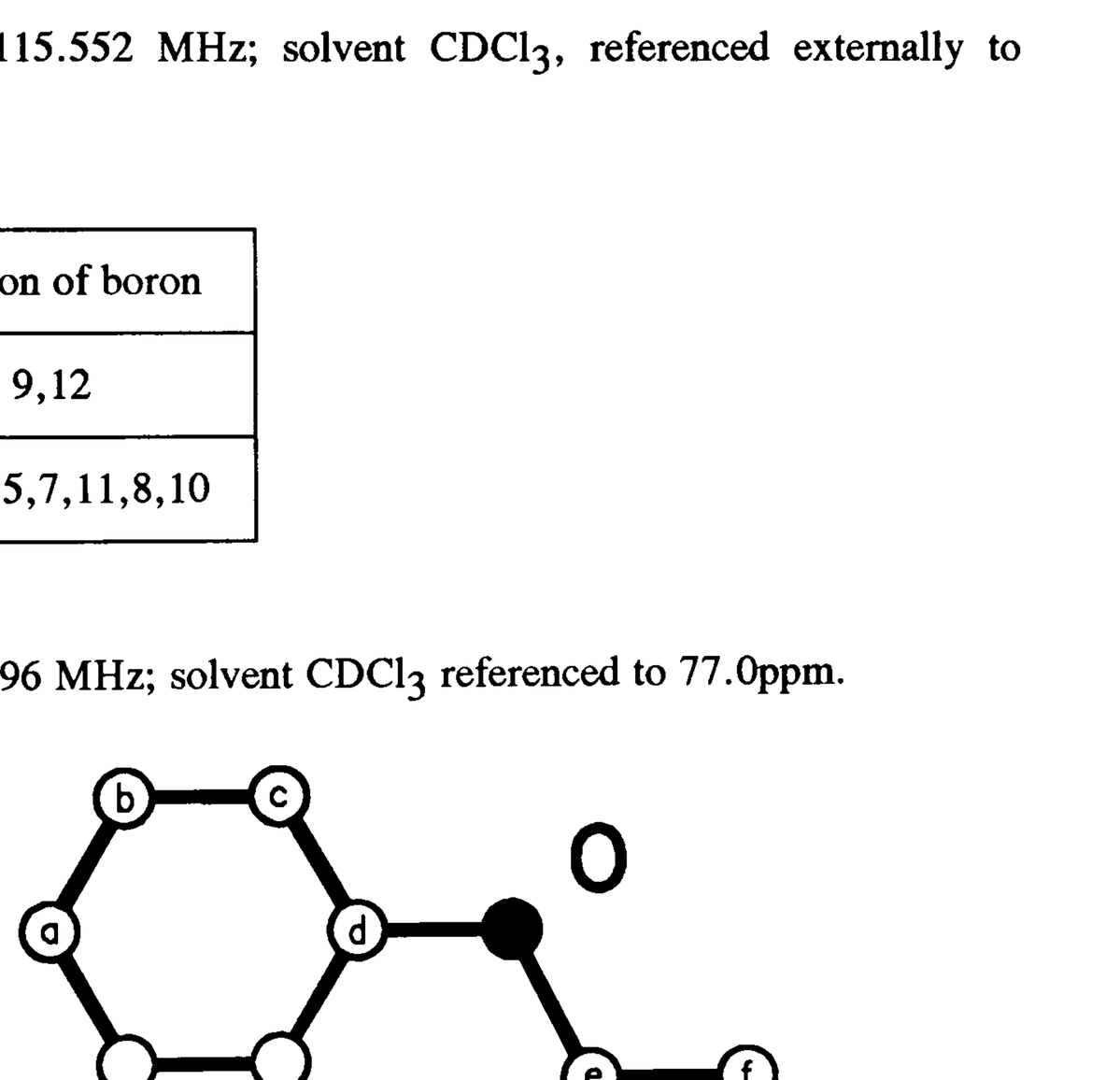
^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.39-7.13	10	multiplet	aromatic C(a,b,c)-H
6.96 6.93 6.76 6.73	8	doublet of doublets	aromatic C(f,g)-H
3.8-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

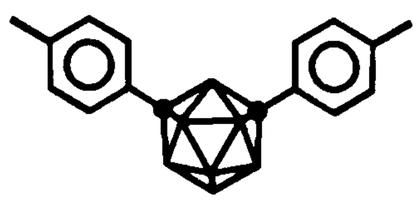
δ_{ppm}	intensity	position of boron
-2.87	2	9,12
-10.67	8	3,6,4,5,7,11,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.



δ_{ppm}	position of carbon
159.29	d
155.76	e
132.33	g
129.95	b
125.12	h
124.33	a
119.69	f
117.46	c
85.35	i

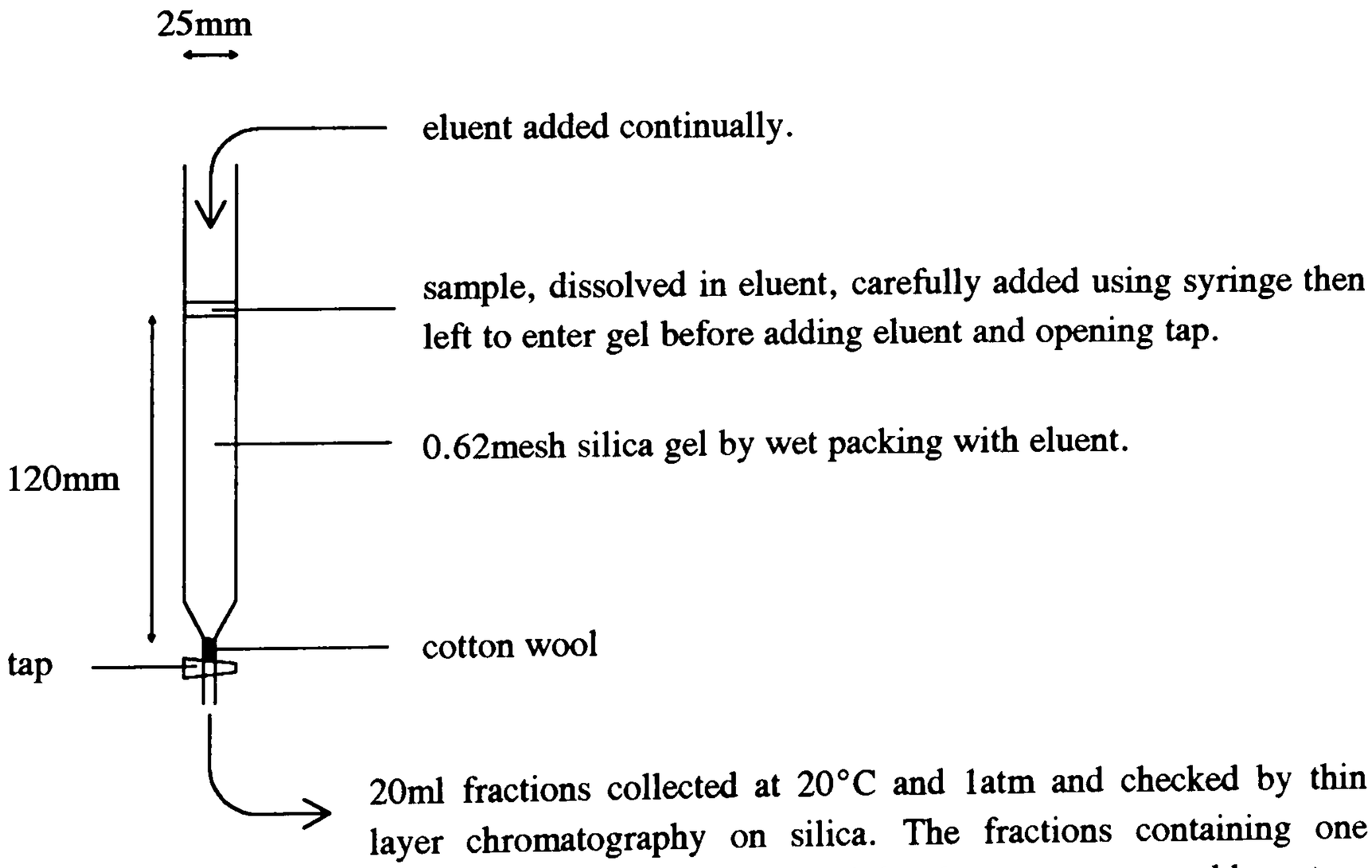
1,7-bis(4-methylphenyl)-1,7-dicarba-*closo*-dodecaborane



METHOD A

A 16mm bore Carius tube (150mm length) was charged with 3.24g (0.01 moles) of 1,2-bis(4-methylphenyl)-*ortho*-carborane and sealed with a blow torch under vacuum. It was put in a steel jacket and heated in a furnace at 400°C for 24 hours. The cooled tube was opened and the contents were extracted with boiling hexane. The extracts were combined and the hexane was removed *in vacuo* to give a solid. The residue was found to contain two isomers by thin layer chromatography on silica with hexane as eluent (R_f values were 0.35 for *meta* and 0.25 for *ortho* isomer). These isomers were separated by column chromatography using approximately 0.15g of mixture per run with hexane as eluent. 1.7g (52.5% conversion) of pure 1,7-bis(4-methylphenyl)-*meta*-carborane was obtained and 0.7g of pure 1,2-bis(4-methylphenyl)-*ortho*-carborane was recovered from 2.8g of the isomer mixture.

Apparatus used for column chromatography



METHOD B

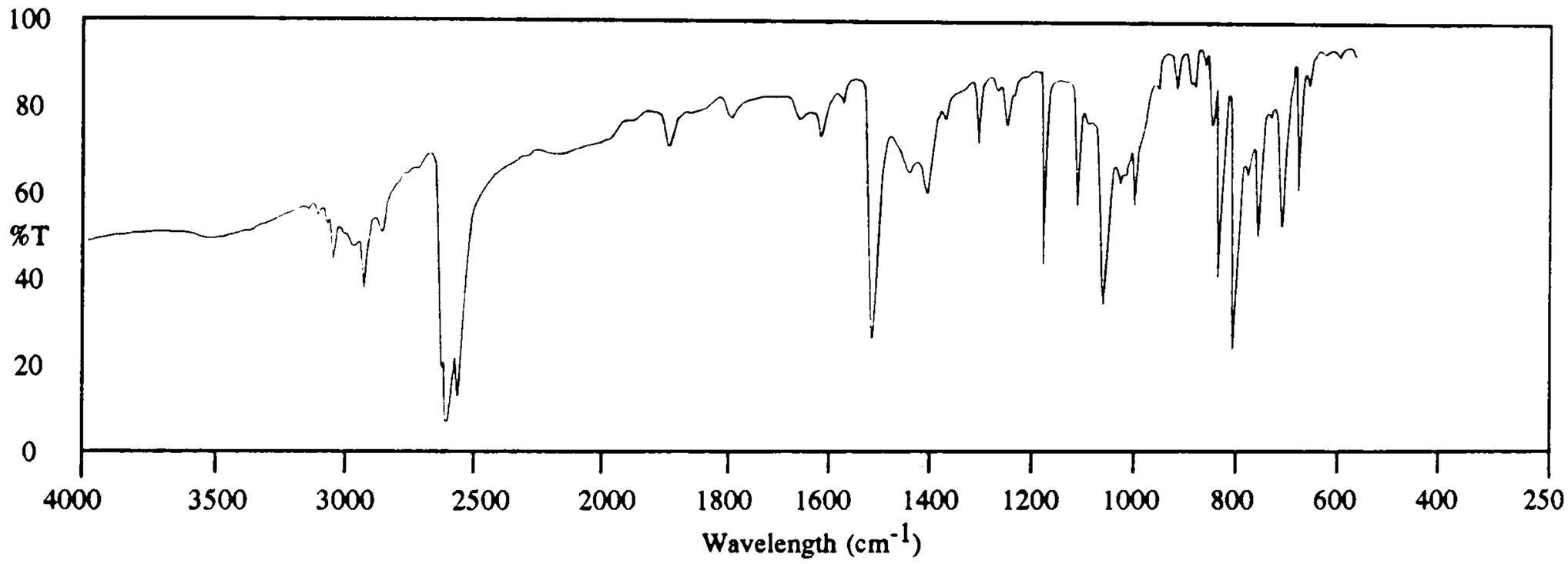
A stirred solution of 2.88g (0.02 moles) *meta*-carborane in 25ml anhydrous diethyl ether was treated dropwise at 0°C with 25ml (0.04 moles) butyllithium in hexane (1.61M) under a dry nitrogen atmosphere. The solution was stirred for 15 minutes at 20°C to produce a white precipitate, cooled to 0°C, diluted with 30ml dry tetrahydrofuran and then in small portions 4.95g (0.05 moles) of anhydrous copper (I) chloride was added. After 15 minutes the solution was stirred for 30 minutes at 20°C then refluxed for 10 minutes. At 0°C, 10.3g (0.05 moles) dry 4-methylbenzenediazonium tetrafluoroborate was added in small portions to the mixture and nitrogen gas was evolved. After 10 minutes stirring at 0°C, the solution was refluxed for 20 minutes, then cooled to 20°C and mixed with 20ml methanol. The precipitate was filtered off, washed with benzene and diethyl ether. The filtrate was washed with dilute hydrochloric acid, water, dried over anhydrous magnesium sulphate and filtered. The solvents in the filtrate were driven off to leave a residue which was dissolved in 30ml absolute alcohol.

The solution was mixed with 15ml of glacial acetic acid, 2ml of concentrated hydrochloric acid and then in small portions 2g of zinc powder was added which gave gas evolution. The decolorized solution was boiled for two minutes, the excess zinc was filtered off and washed with diethyl ether. The filtrate was diluted with water and extracted with diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulphate, filtered, and the ether was driven off by rotary evaporator to yield an off-white solid. The residue was dissolved in hexane, filtered through a short silica gel column and the filtrate was concentrated by removing most of the hexane using a rotary evaporator. 3.05g (47.1%) of white crystals appeared from the concentrated solution which were identified as 1,7-bis(4-methylphenyl)-*meta*-carborane.

Melting point = 140-141°C (lit[3]. =141-142°C)

Analysis Found: C,60.0; H,7.9. $C_{16}H_{24}B_{10}$ requires C,59.3; H,7.4.

Infrared (KBr disc; cm^{-1}) 3132(w), 3098(w), 3063(w), 3041(w), 3002(w), 2965(w), 2924(m), 2859(w), 2637(s), 2613(s), 2576(s), 1901(w), 1786(w), 1649(w), 1613(w), 1573(w), 1514(s), 1447(w), 1412(w), 1378(w), 1317(w), 1278(w), 1261(w), 1250(w), 1192(m), 1131(m), 1111(w), 1082(m), 1054(w), 1041(w), 1026(m), 982(w), 947(w), 928(w), 921(w), 893(w), 878(w), 863(m), 833(s), 809(w), 788(m), 767(w), 742(m), 712(m), 692(w), 667(w), 649(w), 637(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 326 corresponding to the species $^{12}C_{16}{}^{1}H_{24}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 320 and 326. A peak of m/e 91 was present assigned to $CH_3C_6H_4$.

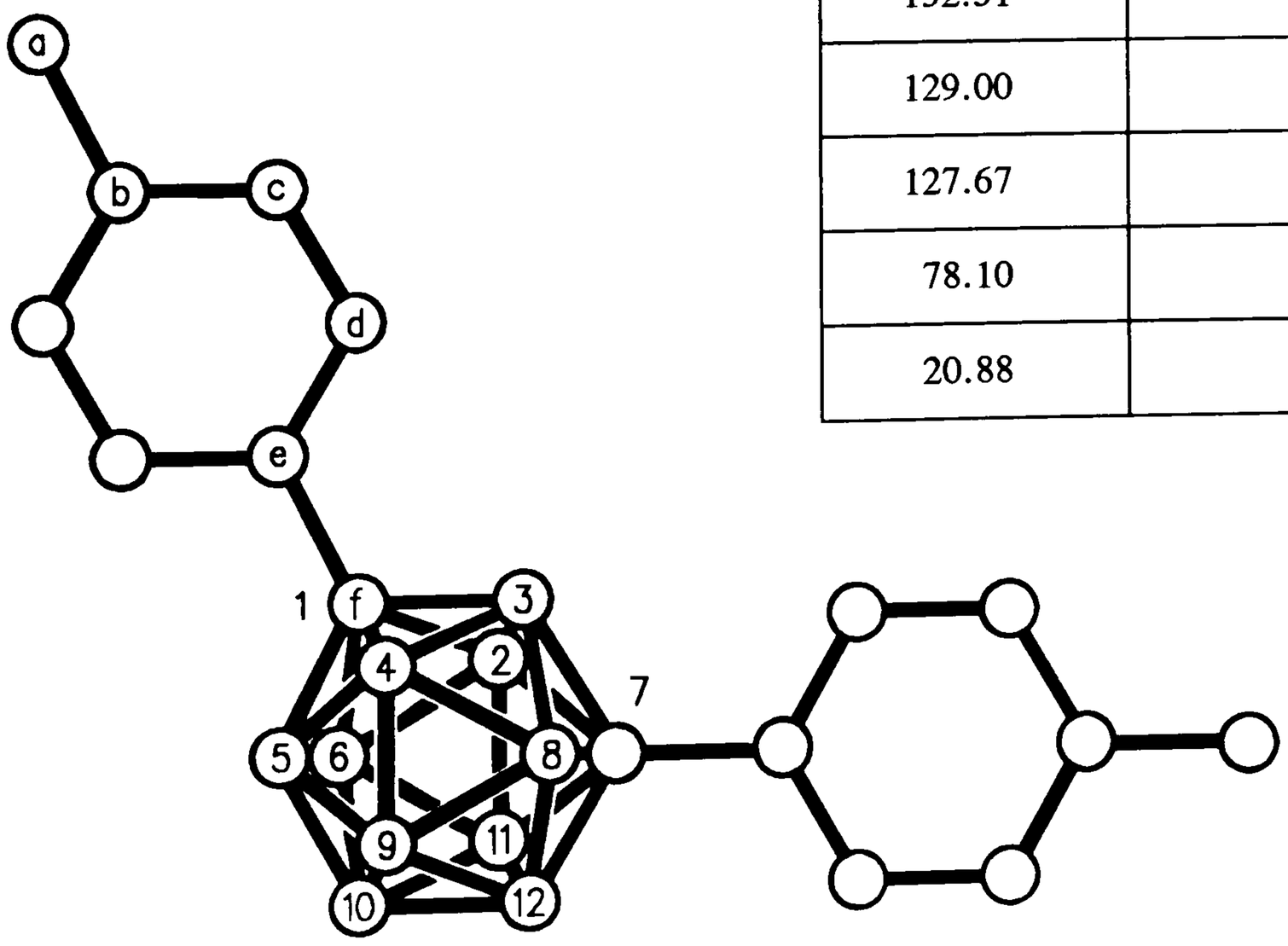
^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.37 7.34 7.09 7.06	8	doublet of doublets	aromatic C(c,d)-H
4.0-1.0	10	broad multiplet	carboranyl B-H
2.32	6	singlet	methyl C(a)-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

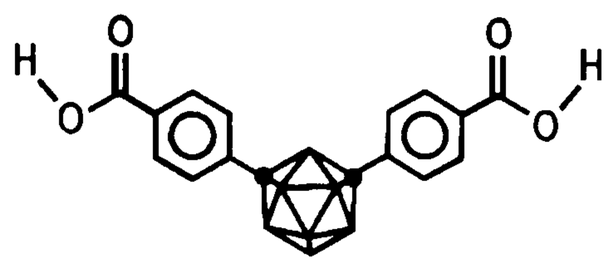
δ_{ppm}	intensity	position of boron
-5.72	2	5,12
-10.30	6	4,6,8,11,9,10
-12.74	2	2,3

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.



δ_{ppm}	position of carbon
138.69	b
132.51	e
129.00	d
127.67	c
78.10	f
20.88	a

1,7-bis(4-carboxyphenyl)-1,7-dicarba-*closo*-dodecaborane

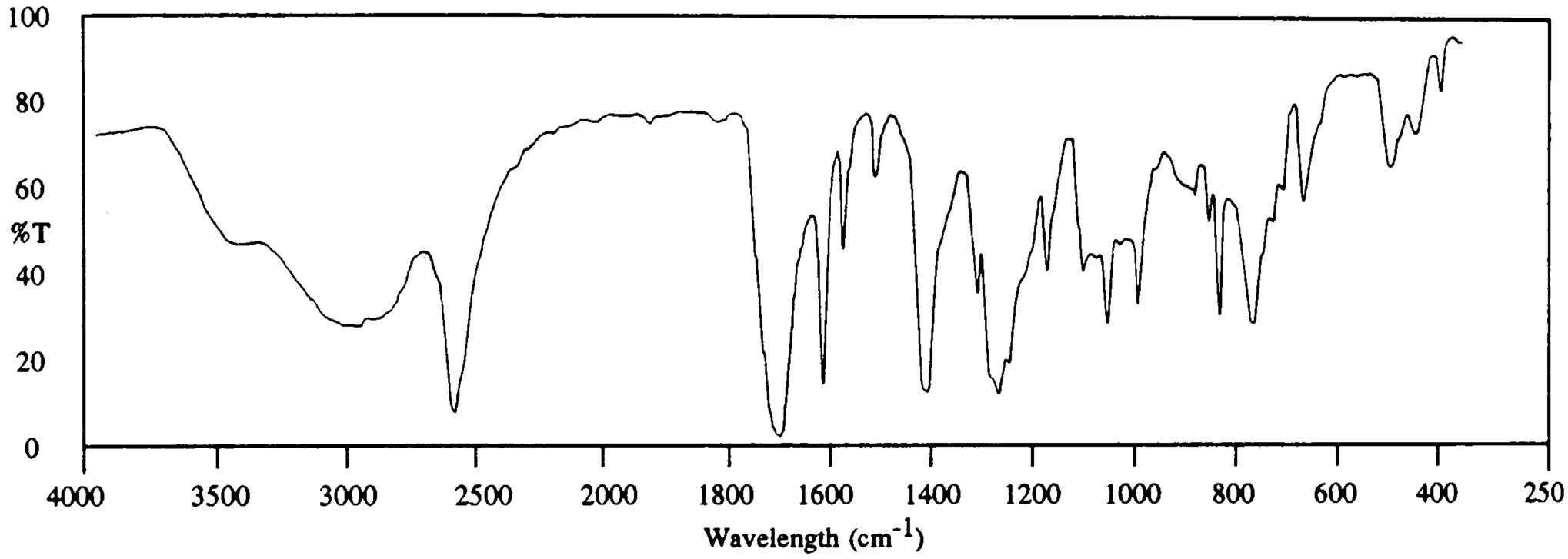


3g (30 mmoles) of chromium trioxide was added in small portions to a stirred mixture of 1.15g (3 mmoles) 1,7-bis(4-methylphenyl)-*meta*-carborane, 50ml glacial acetic acid, 20ml acetic anhydride and 3ml concentrated sulphuric acid. The dark green mixture was stirred at 20°C for two hours then poured into 300ml distilled water. A precipitate slowly appeared which was filtered off and washed well with distilled water to remove the green chromium residues. The off-white solid was dissolved in boiling sodium hydrogen carbonate solution, some undissolved material was filtered off and the solution was acidified with dilute hydrochloric acid to produce a white precipitate. The precipitate was filtered off and recrystallized from an acetone : water mixture to yield 0.72g (56.3%) of 1,7-bis(4-carboxyphenyl)-*meta*-carborane.

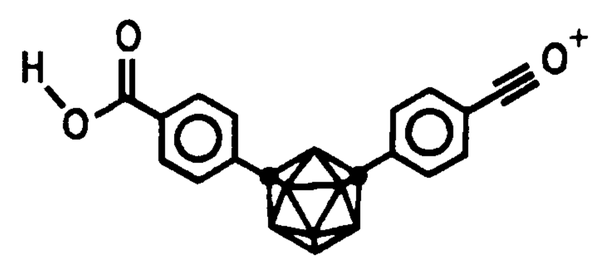
Melting point = 282-284°C (lit[3]. = 281-282°C)

Analysis Found: C,50.1; H,5.4. $C_{16}H_{20}B_{10}O_4$ requires C,50.0; H,5.3.

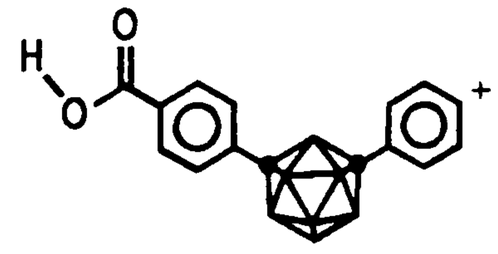
Infrared (KBr disc; cm^{-1}) 3700-2200(m,br), 2604(s), 1939(w), 1808(w), 1700(s), 1612(s), 1577(m), 1566(w), 1516(w), 1422(s), 1418(s), 1311(m), 1294(s), 1281(s), 1253(s), 1226(m), 1220(m), 1191(m), 1124(m), 1078(m), 1056(w), 1021(m), 981(w), 967(w), 962(w), 946(w), 928(w), 917(w), 911(w), 882(w), 863(m), 835(w), 802(m), 794(m), 776(m), 761(w), 738(w), 700(w), 671(w), 637(w), 620(w), 579(w), 533(w), 517(w), 483(w), 434(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 386 corresponding to the species $^{12}C_{16}{}^{1}H_{20}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 380 and 386. Two group of peaks were also seen assigned as:



m/e 363-369



m/e 335-341

^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

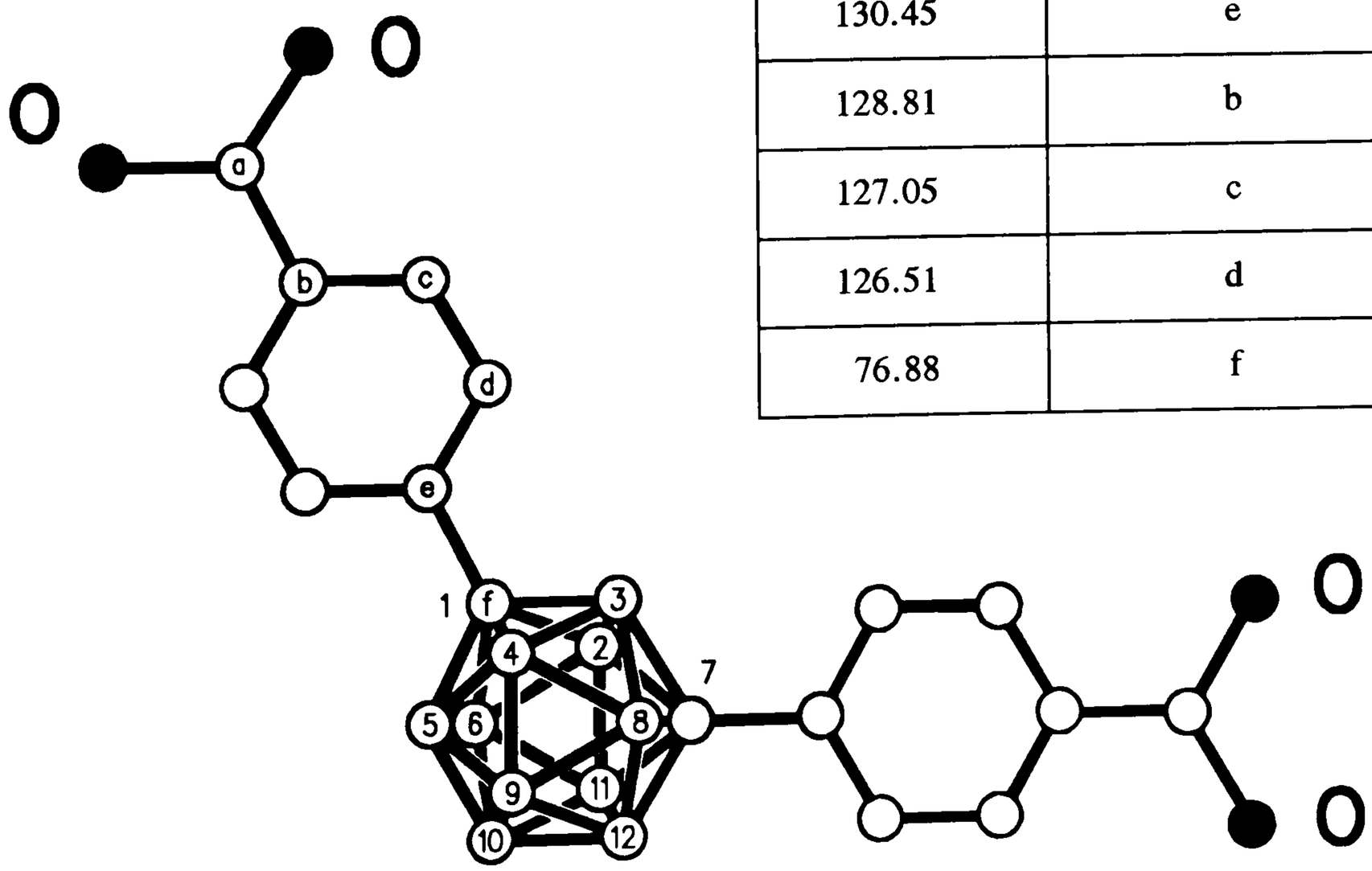
δ_{ppm}	intensity	type of peak	position of proton
8.04 8.01 7.74 7.71	8	doublet of doublets	aromatic C(c,d)-H
7.17	2	broad singlet	O-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

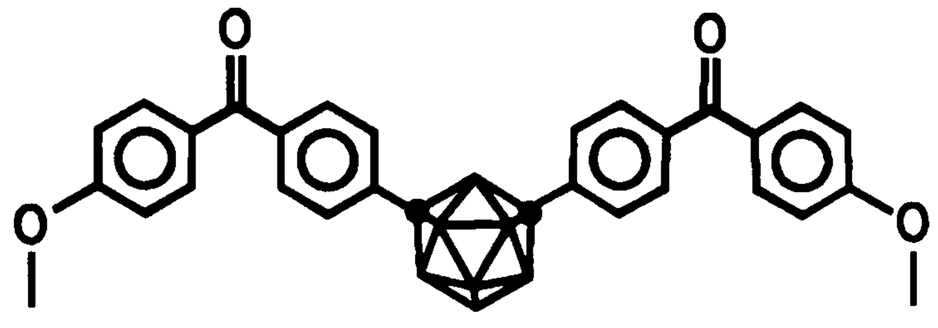
δ_{ppm}	intensity	position of boron
-4.91	2	5,12
-9.57	8	2,3,4,8,6,11,9,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$ referenced to 28.0ppm.

δ_{ppm}	position of carbon
164.98	a
130.45	e
128.81	b
127.05	c
126.51	d
76.88	f



1,7-bis(4′-methoxy-4-benzoylphenyl)-1,7-dicarba-*closo*-dodecaborane

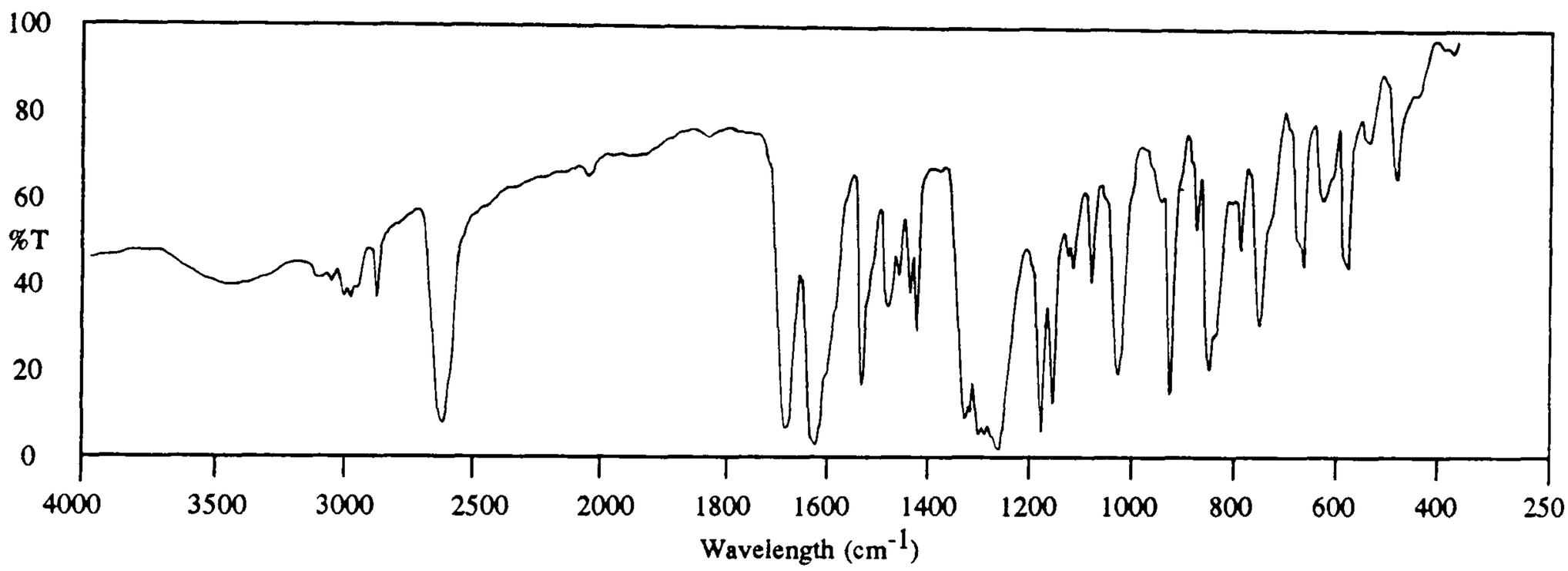


0.384g (1 mmole) 1,7-bis(4-carboxyphenyl)-*meta*-carborane and 0.24g (2.2 mmoles) anisole were dissolved in 5ml of TFSA and left to stand for 32 hours under nitrogen. The dark red solution was poured into 20ml distilled water affording a white precipitate which was extracted with two 10ml portions of diethyl ether. The combined ether extracts were washed with 10% sodium hydroxide and water, dried over anhydrous magnesium sulphate and filtered. The ether was removed by rotary evaporator to leave a yellow solid which was recrystallized from hexane to give 0.38g (67.6%) of 1,7-bis(4′-methoxy-4-benzoylphenyl)-*meta*-carborane.

Melting point = 104-105°C

Analysis Found: C,63.7; H,5.8. $C_{30}H_{32}B_{10}O_4$ requires C,64.1; H,5.7.

Infrared (KBr disc; cm^{-1}) 3090(w), 3058(w), 3015(w), 2977(w), 2941(w), 2920(w), 2847(w), 2608(s), 2058(w), 1659(s), 1610(s), 1602(s), 1581(m), 1564(m), 1512(m), 1502(m), 1493(w), 1463(m), 1461(m), 1442(w), 1420(w), 1408(m), 1318(s), 1308(s), 1290(s), 1280(s), 1277(s), 1267(s), 1254(s), 1247(s), 1192(w), 1173(s), 1150(s), 1124(w), 1115(w), 1113(w), 1079(w), 1057(w), 1049(w), 1029(m), 979(w), 972(w), 965(w), 949(w), 930(s), 911(w), 889(w), 871(w), 857(m), 848(m), 844(m), 813(w), 798(w), 762(m), 741(w), 709(w), 688(w), 680(m), 643(w), 631(w), 602(m), 596(m), 557(w), 504(w), 481(w), 466(w), 461(w), 425(w), 420(w), 397(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 564 corresponding to the species $^{12}C_{30}{}^{1}H_{32}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 558 and 564.

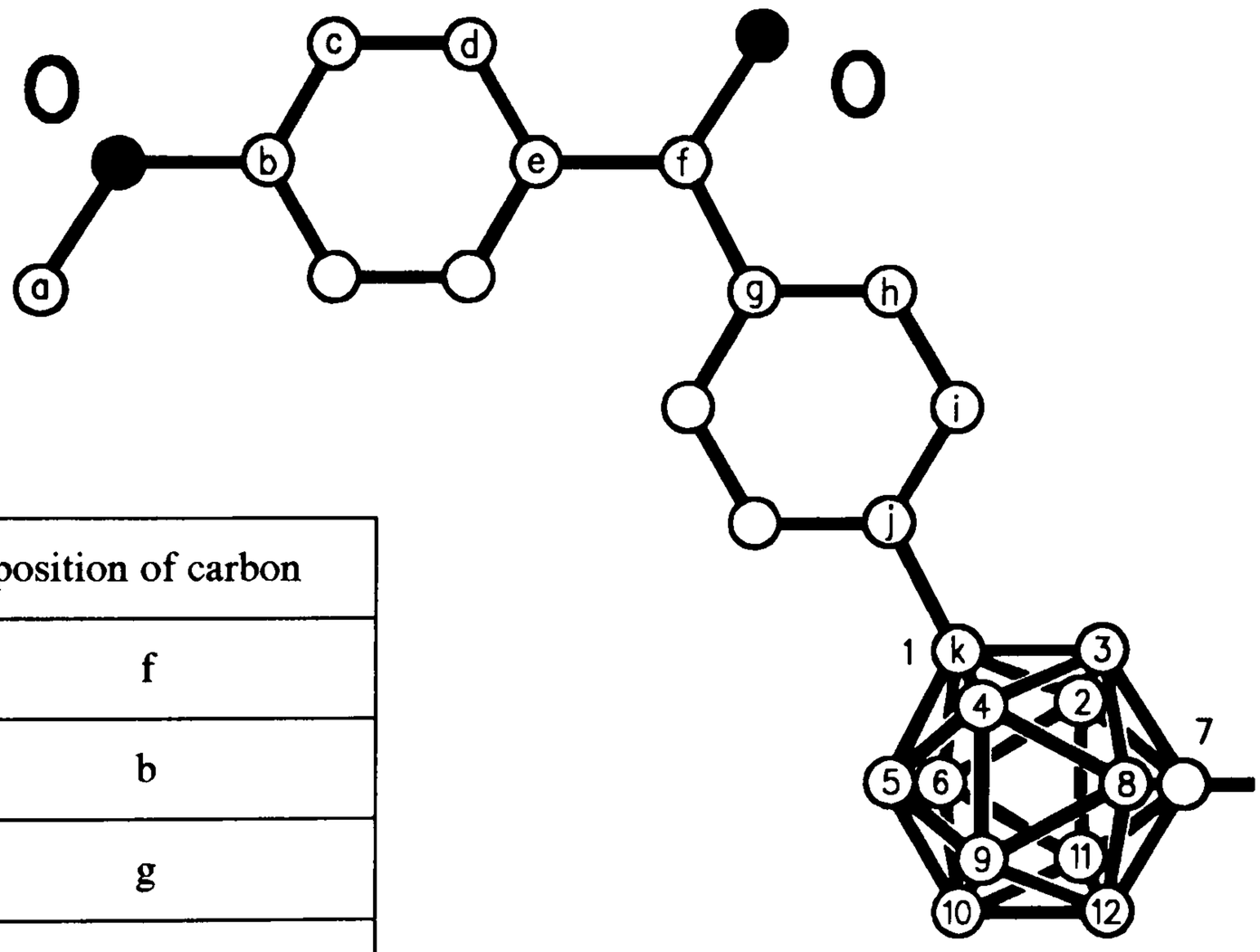
^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.82 7.79 6.98 6.95	8	doublet of doublets	aromatic C(c,d)-H
7.68 7.65 7.60 7.57	8	doublet of doublets	aromatic C(h,i)-H
3.89	6	singlet	methyl C-H
3.9-1.1	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

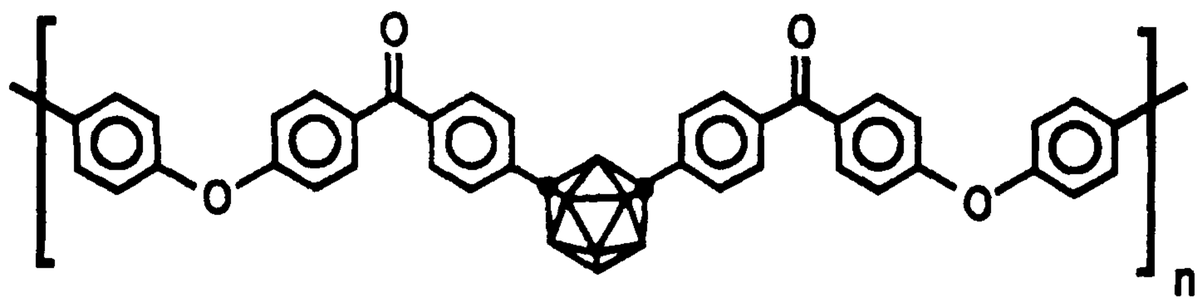
δ_{ppm}	intensity	position of boron
-4.82	2	5,12
-9.96	8	2,3,4,8,6,11,9,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.



δ_{ppm}	position of carbon
194.45	f
163.54	b
138.65	g
137.80	j
132.52	d,e
129.67	i
127.82	h
113.72	c
77.12	k
55.51	a

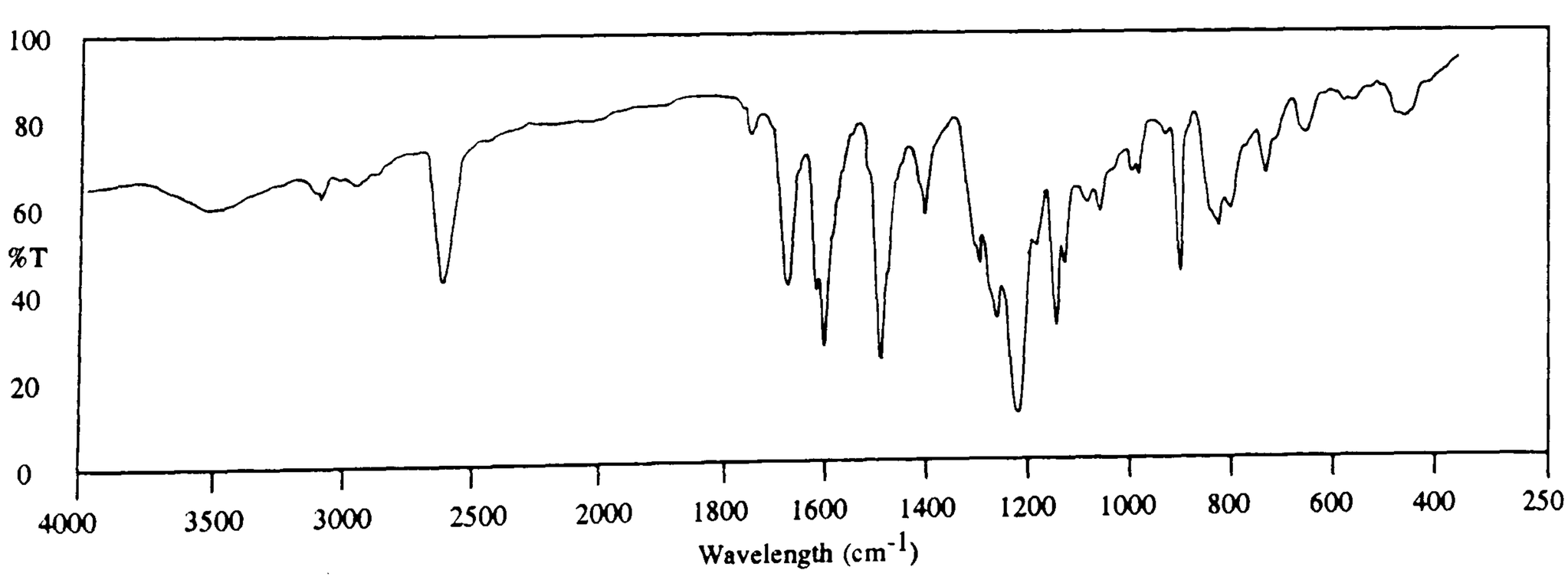
1,7-bis(4-carboxyphenyl)-1,7-dicarba-*closo*-dodecaborane - 4,4′-diphenoxybiphenyl polymer



0.384g (1 mmoles) 1,7-bis(4-carboxyphenyl)-*meta*-carborane and 0.338g (1 mmoles) 4,4′-diphenoxybiphenyl were dissolved in 10ml of TFSA and left to stand for 26 hours under nitrogen. The dark red solution was poured into 30ml distilled water affording an off-white precipitate. The solid was filtered off, thoroughly washed with 10% sodium hydroxide and water and dried in an oven at 100°C to give 0.62g (80.3%) of 1,7-bis(4-carboxyphenyl)-*meta*-carborane - 4,4′-diphenoxybiphenyl polymer.

Analysis Found: C,68.2; H,4.8. $(C_{40}H_{34}B_{10}O_4)_n$ requires C,70.0; H,5.0.

Infrared (KBr disc; cm^{-1}) 3080(w), 3072(w), 3046(w), 2611(s), 2590(s), 1662(s), 1658(s), 1609(s), 1596(s), 1563(w), 1492(s), 1457(w), 1415(w), 1409(w), 1359(w), 1316(m), 1309(m), 1284(s), 1278(s), 1239(s), 1201(m), 1167(s), 1150(m), 1124(w), 1110(w), 1107(w), 1103(w), 1079(w), 1020(w), 1014(w), 1007(w), 967(w), 953(w), 930(s), 911(w), 889(w), 870(m), 855(m), 833(m), 830(m), 797(w), 786(w), 759(m), 747(w), 741(w), 715(w), 689(w), 681(w), 670(w), 649(w), 637(w), 612(w), 588(w), 562(w), 535(w), 507(w), 492(w), 483(w).



^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

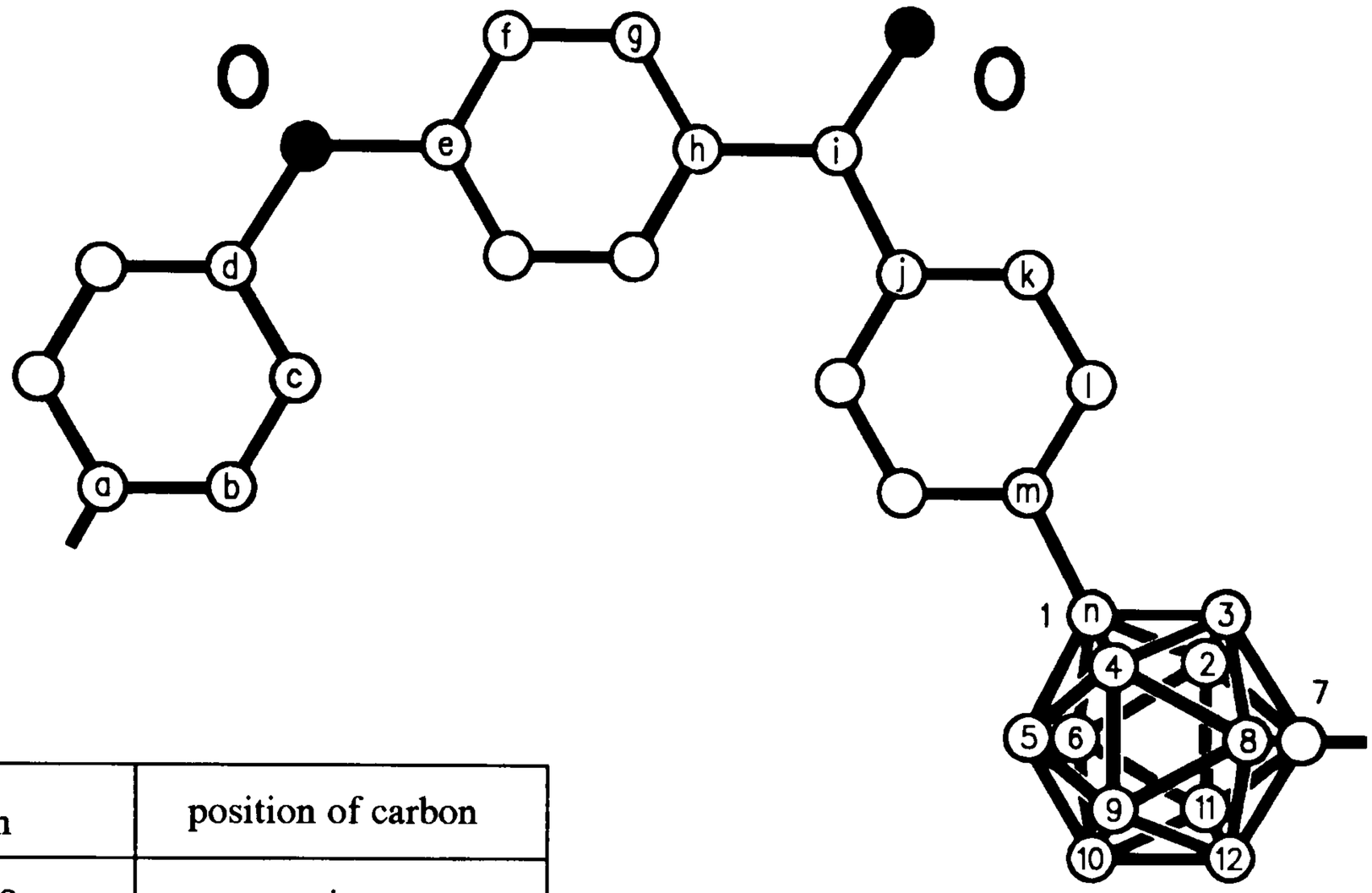
δ_{ppm}	intensity	type of peak	position of proton
7.75 7.72 7.01 6.98	4	doublet of doublets	aromatic C-H
7.63 7.60 7.10 7.07	4	doublet of doublets	aromatic C-H
7.53* 7.51*	4	doublet of doublets	aromatic C-H
3.5-2.5	10	broad multiplet	carboranyl B-H

* poor peak resolution

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-4.92	2	5,12
-9.92	8	2,3,4,6,8,11,9,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

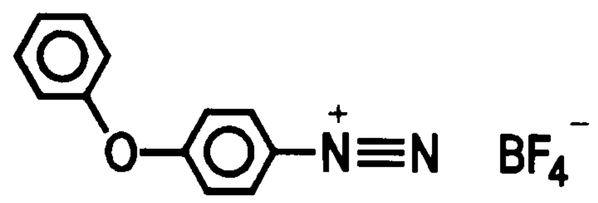


δ_{ppm}	position of carbon
194.18	i
161.73	e
155.00	d
138.59	j
138.27	m
136.75	a
132.44	g
131.56	h
129.73	l
128.54	k
127.87	b
120.43	c
117.35	f
77.42	n

Attempted formation of 1,7-bis(4-phenoxyphenyl)-1,7-dicarba-*closo*-dodecaborane by thermal isomerization of 1,2-bis(4-phenoxyphenyl)-1,2-dicarba-*closo*-dodecaborane

A 16mm bore 120mm Carius tube was charged with 2.4g (0.005 moles) of 1,2-bis(4-phenoxyphenyl)-*ortho*-carborane and sealed with a blow torch under vacuum. It was put in a steel jacket and heated in a furnace at 400°C for 24 hours. The tube was cooled then opened in a fume hood and the contents were extracted with boiling hexane. The extracts were combined and the hexane was removed *in vacuo* to give a solid which was found to contain only the starting carborane material by ^{13}C n.m.r. spectroscopy (carboranyl C peak at 85ppm for *ortho* isomer and at 77ppm for *meta* in $(CD_3)_2CO$). The same procedure was attempted at 460°C and again the solid was found to contain only the *ortho* isomer. It was repeated at 520°C for 24 hours and after cooling at room temperature the tube showed considerable pressure build up as a loud sound was heard when opened. An insoluble glassy material was obtained identified as polymeric matter by infrared spectroscopy.

4-phenoxybenzenediazonium tetrafluoroborate



18.5g (0.1 moles) of 4-phenoxyaniline was dissolved in 125ml of 1:1 hydrochloric acid : water with stirring for 30 minutes. At 0°C, 7g (0.101 moles) of sodium nitrite in 15ml water was added in small portions to the solution and stirred for an hour. A chilled solution of 11.2g (0.102 moles) sodium tetrafluoroborate in 30ml water was added dropwise to the mixture with the temperature still at 0°C and stirred vigorously for 30 minutes. The solid was filtered off, washed with iced water, methanol and diethyl ether, and dried *in vacuo* to yield 23.3g (82.1%) of 4-phenoxybenzenediazonium tetrafluoroborate.

Melting point = decomposed at 101°C

Analysis Found: C,50.6; H,3.1; N,9.8. $C_{12}H_9BF_4N_2O$ requires C,50.7; H,3.2; N,9.9.

Infrared (Nujol mull; cm^{-1}) 3118(m), 3073(w), 3041(w), 2961(s), 2938(s), 2861(s), 2674(w), 2274(m), 2227(m), 1598(m), 1575(s), 1571(s), 1485(s), 1478(s), 1470(s), 1459(s), 1444(m), 1379(w), 1368(w), 1338(w), 1307(w), 1280(s), 1192(m), 1177(w), 1158(w), 1127(m), 1098(s), 1068(s), 1050(s), 1030(s), 1004(m), 974(w), 930(w), 872(m), 854(w), 842(m), 818(w), 807(m), 772(m), 769(m), 734(w), 721(w), 703(m), 698(w), 642(w), 613(w), 527(w), 515(w), 501(w), 472(w), 430(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 188 corresponding to the species $^{12}C_{12}{}^{1}H_9{}^{19}F{}^{16}O$ as a result of decomposition of the salt. A peak of m/e 77 was seen and identified as C_6H_5.

^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2CO$ referenced to 2.05ppm.

δ_{ppm}	intensity	type of peak	position of proton
8.80 8.77 7.32 7.29	4	doublet of doublets	aromatic C(f,g)-H
7.62-7.39	5	multiplet	aromatic C(a,b,c)-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2CO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

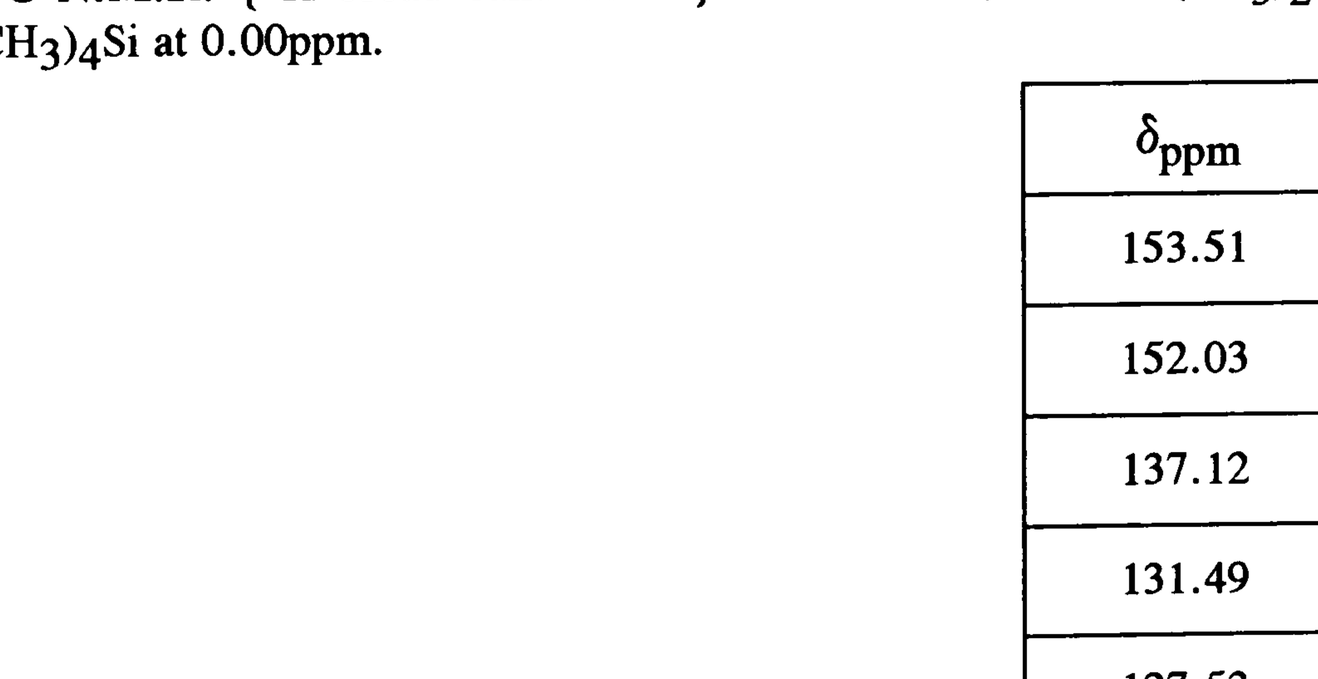
δ_{ppm}	position of boron
-0.16	B-F

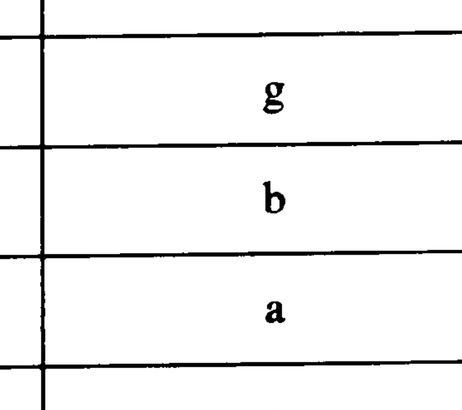
^{19}F N.M.R. {^{1}H broad band noise } 235.342 MHz solvent $(CD_3)_2CO$, referenced externally to $CFCl_3$ at 0.00ppm.

δ_{ppm}	position of fluorine
-150.50	B-F

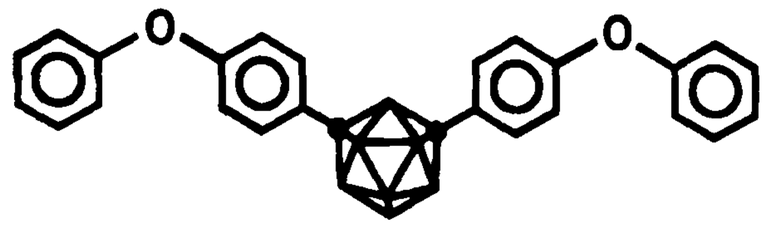
^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $(CD_3)_2CO$, referenced externally to $(CH_3)_4Si$ at 0.00ppm.

δ_{ppm}	position of carbon
153.51	e
152.03	d
137.12	g
131.49	b
127.53	a
121.57	c
119.67	f
105.82	h





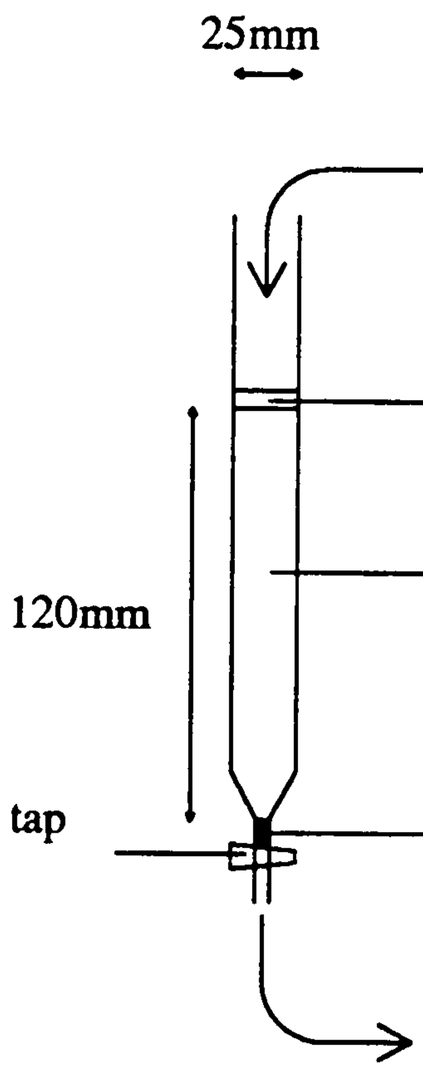
1,7-bis(4-phenoxyphenyl)-1,7-dicarba-*closo*-dodecaborane



A stirred solution of 2.88g (0.02 moles) *meta*-carborane in 25ml anhydrous diethyl ether was treated dropwise with 25ml (0.04 moles) butyllithium in hexane (1.61M) at 0°C under a dry nitrogen atmosphere. The solution was stirred for 15 minutes at 20°C giving a white precipitate. It was cooled to 0°C, diluted with 30ml dry tetrahydrofuran and then, in small portions, 4.95g (0.05 moles) of anhydrous copper (I) chloride was added. After 15 minutes the solution was stirred for 30 minutes at 20°C then refluxed for 10 minutes. At 0°C, 14.2g (0.05 moles) dry 4-phenoxybenzenediazonium tetrafluoroborate was added to the solution in small portions where nitrogen gas was evolved. After 10 minutes stirring at 0°C, the solution was refluxed for 20 minutes, then cooled to 20°C, mixed with 20ml methanol and left to stir for 30 minutes.

The precipitate formed was filtered off, washed with benzene, diethyl ether and discarded. The green filtrate was washed with dilute hydrochloric acid and water, dried over anhydrous magnesium sulphate and filtered. Solvents were driven off the filtrate to leave an oily residue which was dissolved in 30ml absolute alcohol. The orange solution was mixed with 15ml of glacial acetic acid, 2ml of concentrated hydrochloric acid and then 2g of zinc powder was added in small portions which gave gas evolution. The decolorized solution was boiled for two minutes then the excess zinc was filtered off and washed with diethyl ether. The filtrate was diluted with water and extracted with diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulphate, filtered, and the ether was driven off by rotary evaporator leaving an oil. The residue was found to contain two main compounds identified as diphenyl ether and a new product by thin layer chromatography with hexane as eluent. The oil was vacuum distilled to remove most of the diphenyl ether and the undistilled residue was subject to two runs, 2.2g per run, of column chromatography with hexane as eluent to give 3.95g (41.1%) of 1,7-bis(4-phenoxyphenyl)-*meta*-carborane.

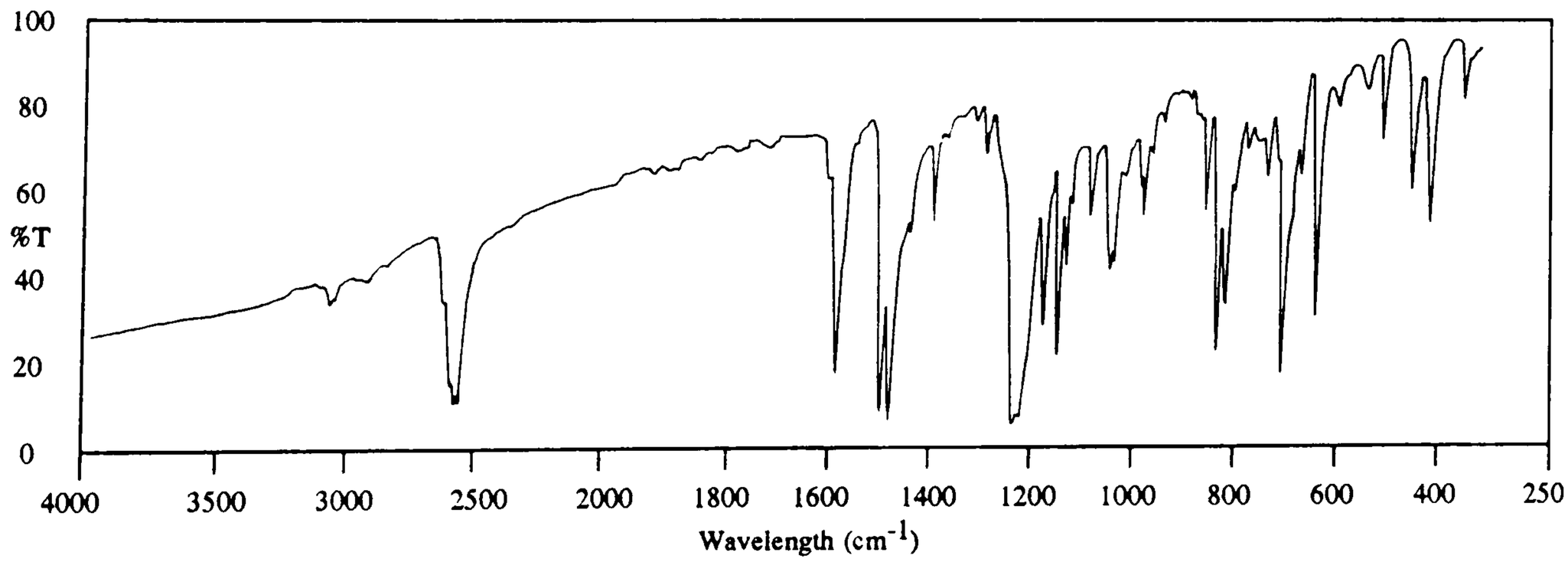
Apparatus used for column chromatography



Melting point = 110-111°C

Analysis Found: C,64.7; H,5.7. $C_{26}H_{28}B_{10}O_2$ requires C,65.0; H,5.4.

Infrared (KBr disc; cm^{-1}) 3104(w), 3079(w), 3071(w), 3062(w), 3048(w), 2646(m), 2618(s), 2602(s), 2587(s), 1613(w), 1593(s), 1508(s), 1492(s), 1470(w), 1459(w), 1412(w), 1387(w), 1332(w), 1312(w), 1309(w), 1282(w), 1256(s), 1247(s), 1233(s), 1203(m), 1177(m), 1162(m), 1154(w), 1118(w), 1081(m), 1074(m), 1057(w), 1038(w), 1023(w), 1018(w), 1005(w), 982(w), 934(w), 917(w), 910(w), 900(w), 877(m), 862(m), 848(w), 822(w), 807(w), 798(w), 783(w), 762(w), 752(m), 742(w), 722(w), 690(m), 668(w), 657(w), 651(w), 635(w), 602(w), 597(w), 569(w), 512(w), 486(w), 478(m), 416(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 482 corresponding to the species $^{12}C_{26}{}^{1}H_{28}{}^{11}B_{10}{}^{16}O_2$, accompanied by the usual carborane isotope distribution pattern between m/e 476 and 482. A peak of m/e 77 was also observed and identified as $C_6H_5{}^{+}$.

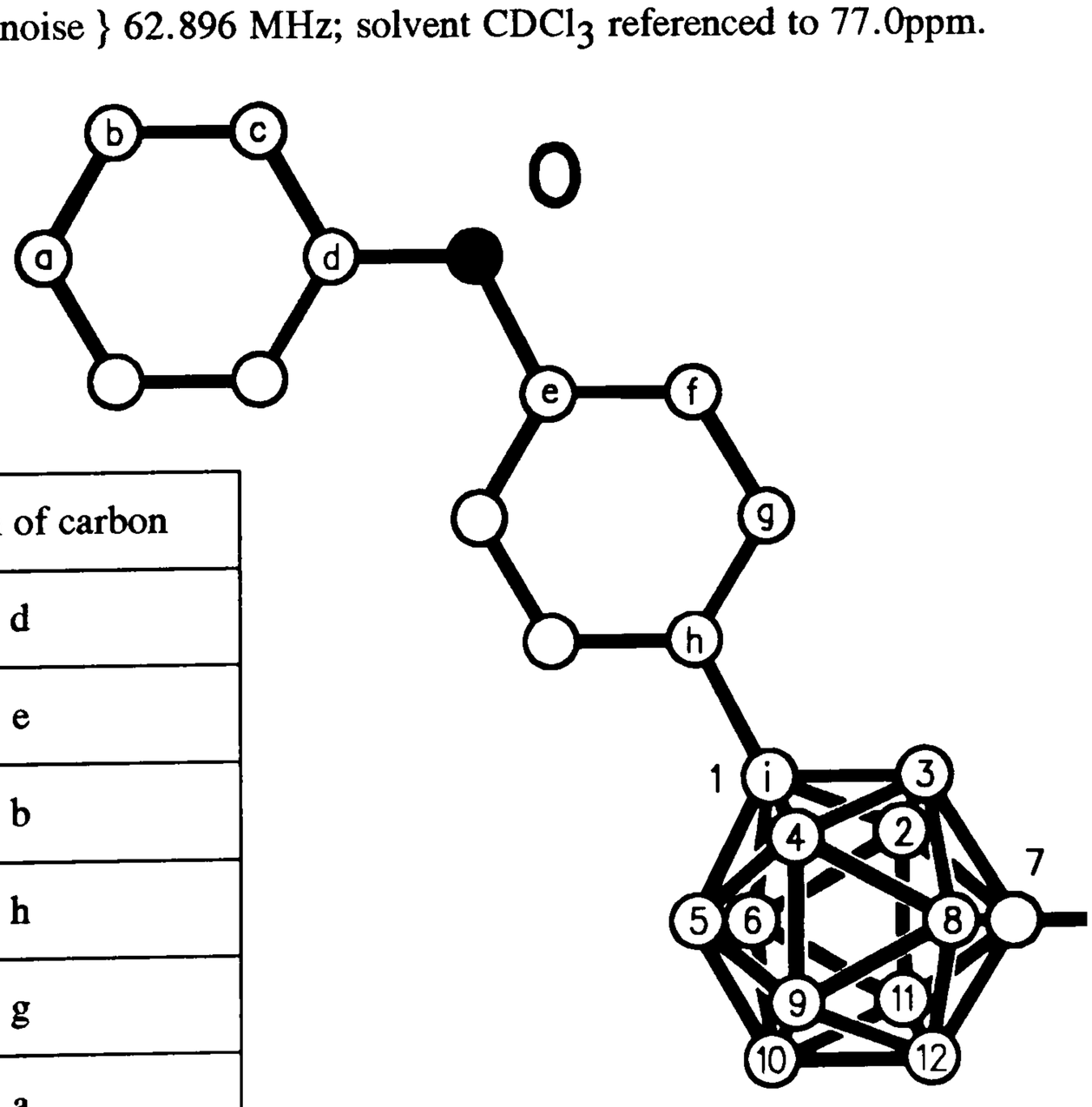
^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.43-7.31	10	multiplet	aromatic C(a,b,c)-H
7.04 7.01 6.88 6.85	8	doublet of doublets	aromatic C(f,g)-H
3.9-1.1	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

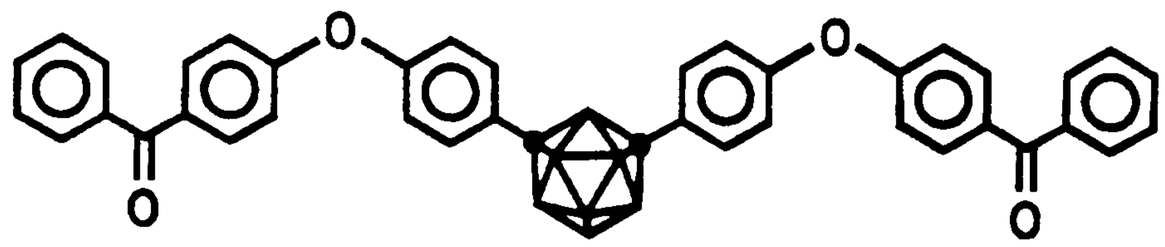
δ_{ppm}	intensity	position of boron
-5.87	2	5,12
-10.20	8	2,3,4,8,6,11,9,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.



δ_{ppm}	position of carbon
158.11	d
156.16	e
129.87	b
129.70	h
129.23	g
123.98	a
119.53	f
117.76	c
77.76	i

1,7-bis(4′-benzoyl-4-phenoxyphenyl)-1,7-dicarba-*closo*-dodecaborane

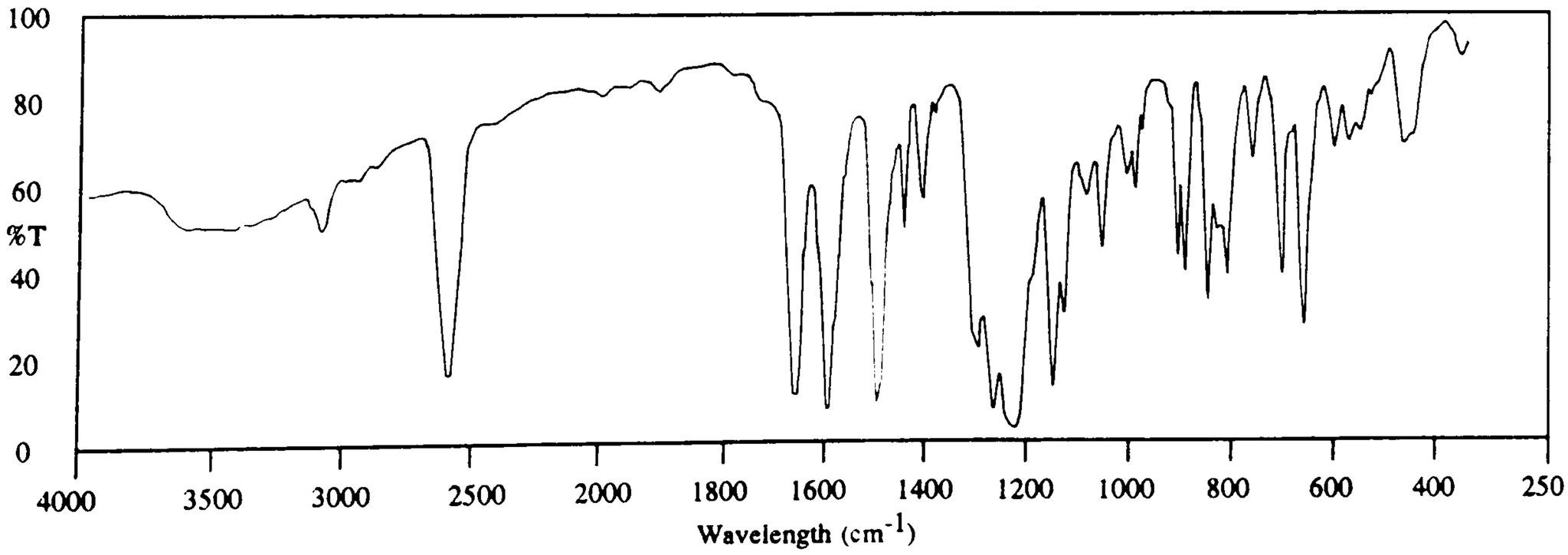


A mixture of 0.24g (0.5mmoles) 1,7-bis(4-phenoxyphenyl)-*meta*-carborane and 0.122g (1 mmole) benzoic acid was dissolved in 10ml TFSA with stirring under a nitrogen atmosphere. The red solution was left to stand for 16 hours and then poured into 25ml distilled water. The resulting precipitate was filtered off, washed with 10% sodium hydroxide and water and dried *in vacuo*. After recrystallization with hexane 0.31g (90.1%) 1,7-bis(4′-benzoyl-4-phenoxyphenyl)-*meta*-carborane was obtained.

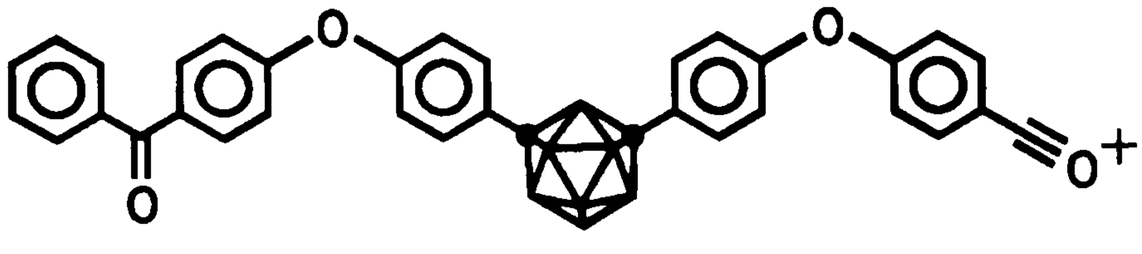
Melting point = 95-96°C

Analysis Found: C,68.4; H,5.6. $C_{40}H_{36}B_{10}O_4$ requires C,69.8; H,5.2.

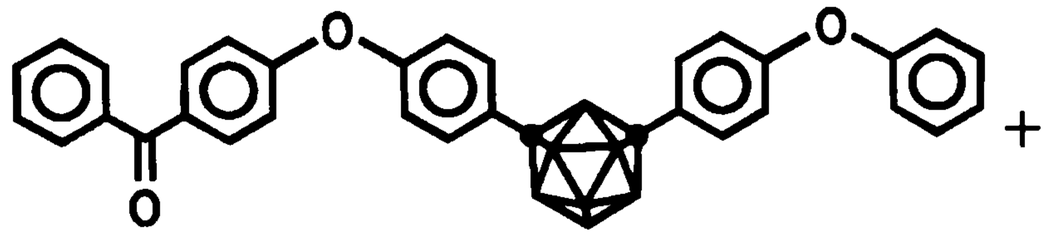
Infrared (KBr disc; cm^{-1}) 3105(w), 3096(w), 3082(w), 3063(w), 3036(w), 2960(w), 2932(w), 2916(w), 2872(w), 2858(w), 2603(s), 2021(w), 1911(w), 1721(w), 1657(s), 1651(s), 1638(m), 1612(m), 1598(s), 1593(s), 1581(m), 1572(m), 1563(w), 1553(w), 1519(w), 1509(m), 1498(s), 1483(s), 1480(w), 1476(w), 1460(w), 1447(w), 1440(w), 1413(w), 1410(w), 1398(w), 1383(w), 1316(s), 1307(s), 1278(s), 1256(s), 1240(s), 1236(s), 1210(m), 1171(s), 1148(m), 1112(w), 1107(w), 1079(w), 1056(w), 1028(w), 1015(w), 1000(w), 950(w), 938(w), 922(m), 890(w), 879(m), 861(w), 842(m), 792(w), 738(m), 718(w), 698(s), 682(w), 668(w), 638(w), 611(w), 590(w), 569(w), 553(w), 507(w), 492(w), 398(w).

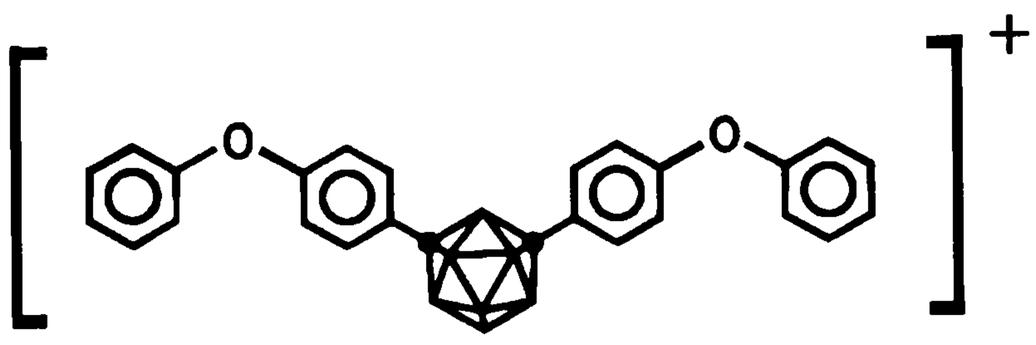


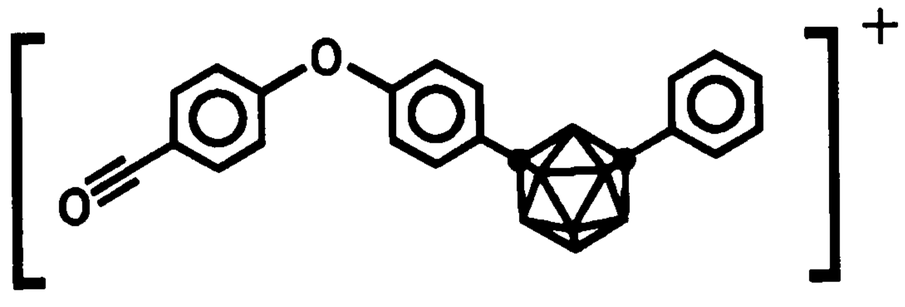
Mass spectrum (E.I.) A highest mass peak was observed at m/e 614 corresponding to the fragment $^{12}C_{32}{}^{1}H_{31}{}^{11}B_{10}{}^{16}O_4$, accompanied by the usual carborane isotope distribution pattern between m/e 609 and 614, assigned to:

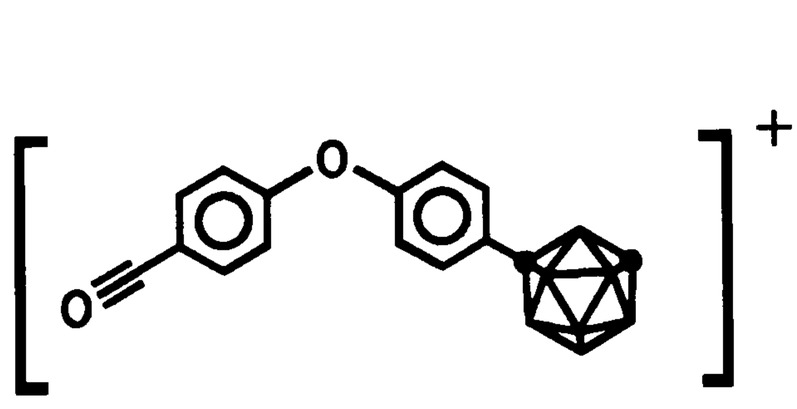


Other peaks seen were assigned to:









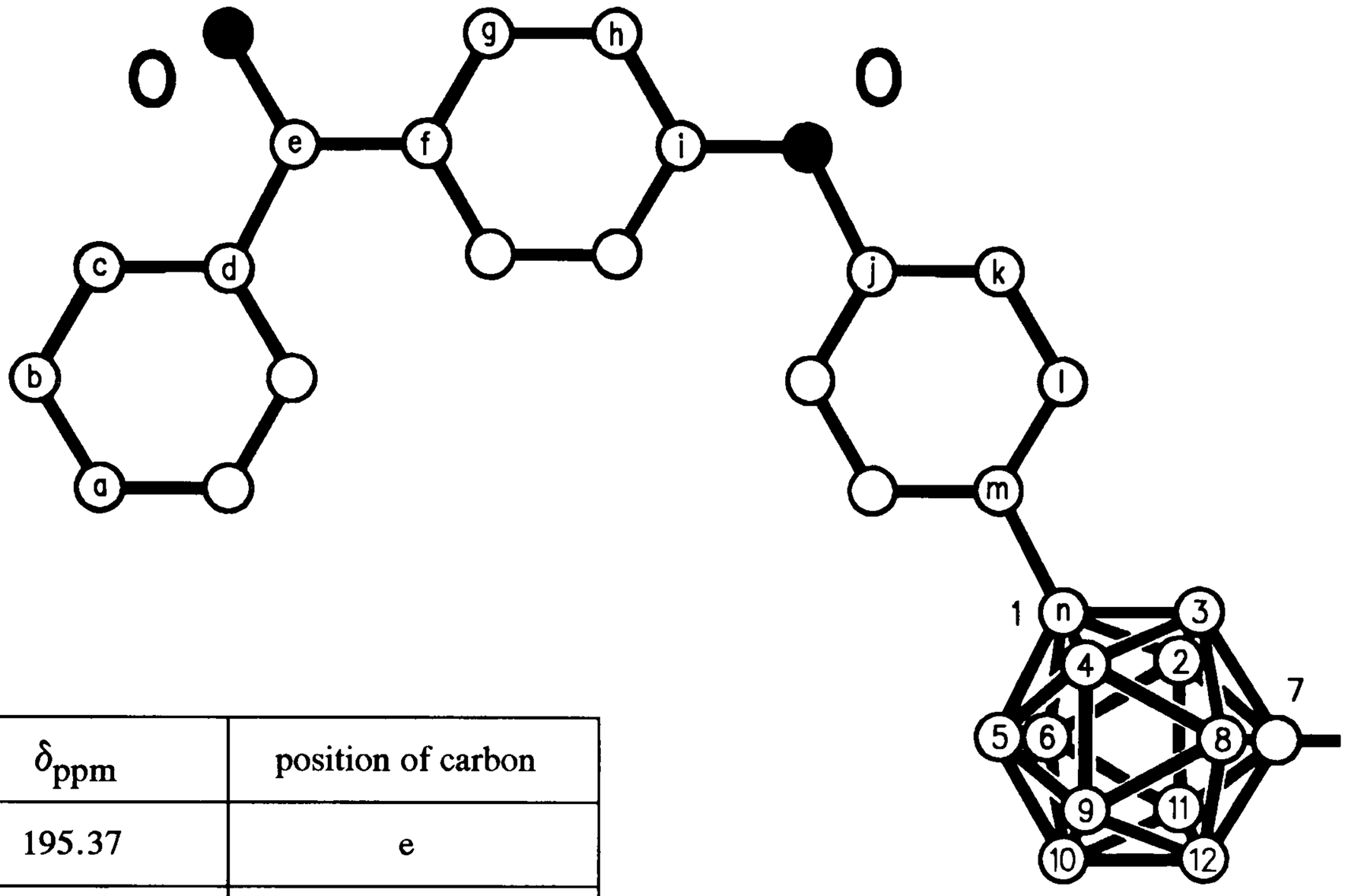
^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.85 7.82 6.99 6.96	8	doublet of doublets	aromatic C-H
7.80 7.77 7.06 7.03	8	doublet of doublets	aromatic C-H
7.56-7.48	10	multiplet	aromatic C(a,b,c)-H
4.1-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-5.91	2	5,12
-10.02	8	2,3,4,6,8,11,9,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.



δ_{ppm}	position of carbon
195.37	e
160.52	i
156.50	j
137.78	d
132.48	l
132.26	a
131.09	f
129.82	c
129.60	g
129.52	m
128.26	b
119.26	h
117.89	k
77.68	n

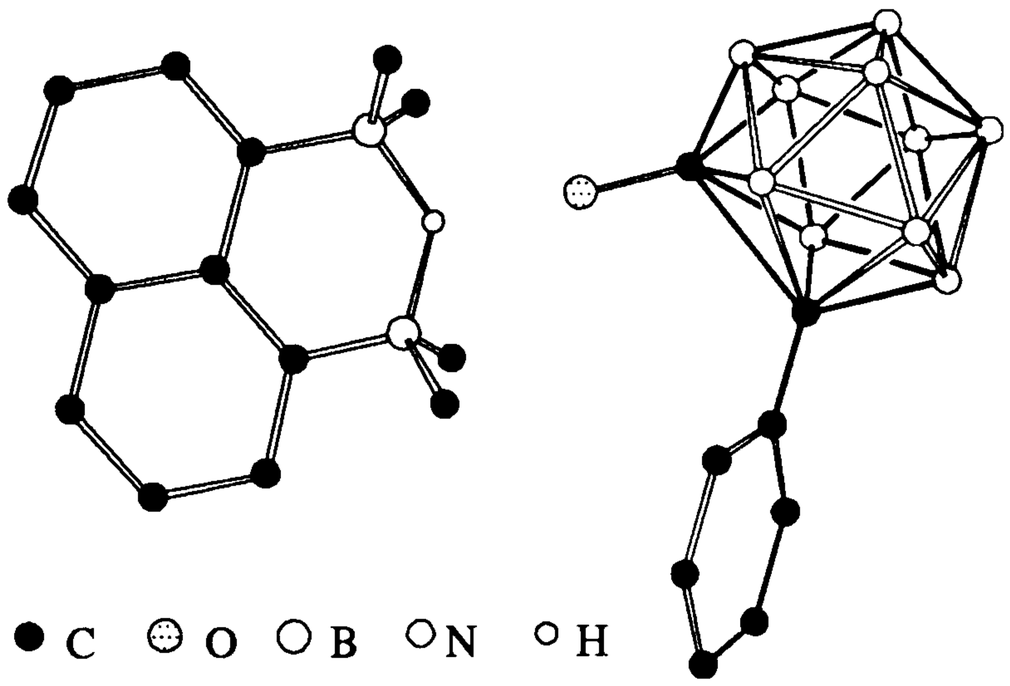
CHAPTER 8

CARBORANE ANIONS AND RELATED COMPOUNDS

This chapter describes the syntheses of some carbon-substituted (-hydroxy, -mercapto, -amino, -diaryl) and boron-substituted (-hydroxy, -decachloro) carboranes carried out in this study. The successful deprotonation of some derivatives with proton sponge and triethylamine and molecular structures of five carborane derivatives determined by X-ray crystallography are included in this chapter.

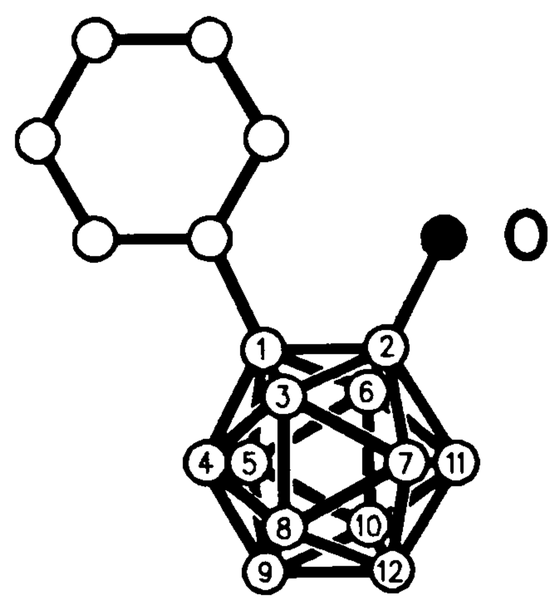
INTRODUCTION

An X-ray study of a salt (**I**) formed by deprotonation of 1-phenyl-2-hydroxy-*ortho*-carborane using proton sponge showed a carborane anion which effectively consists of a *nido*-shaped $PhCB_{10}H_{10}^-$ residue capped by a pentuply-bridging carbonyl group with C−O bond length of 1.245Å[1,2]. The interatomic (B−B, B−C) distances within the polyhedron and ^{11}B and ^{13}C n.m.r. data provided evidence of charge delocalization in the anion into the (electron-deficient) polyhedron leading to C−O π-bonding as illustrated overleaf.

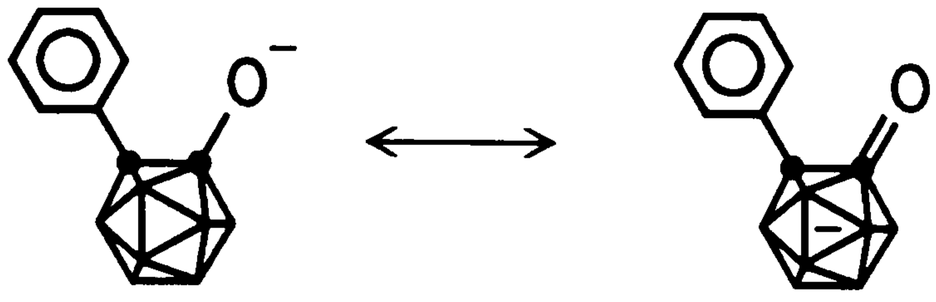


X-ray structure of **I**, $[PhCB_{10}H_{10}CO]^-$ $[C_{10}H_6(NMe_2)_2H]^+$

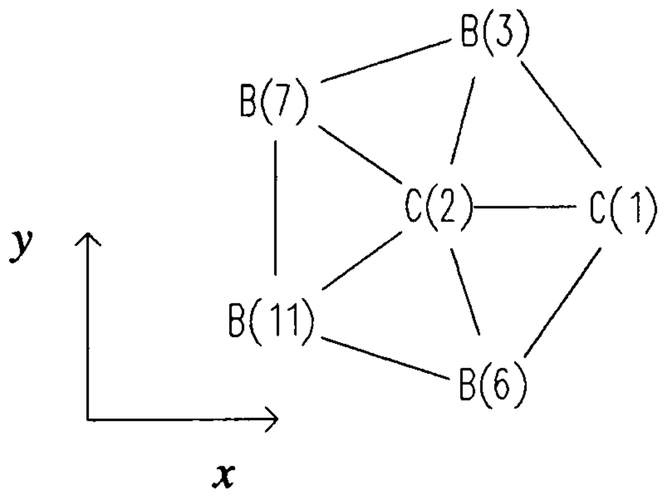
Bond Length	Å
C(2)-O	1.245
C(1)-C(2)	2.001
C(2)-B(3)	1.813
C(2)-B(7)	1.684
C(2)-B(11)	1.683
C(2)-B(6)	1.820
Angle	**°**
C(1)-C(2)-O	117.7

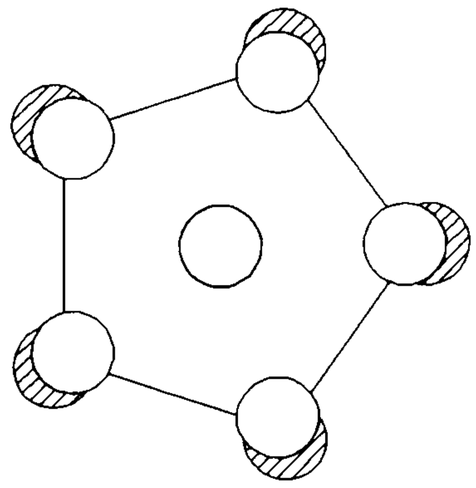


1. Brown D.A. Clegg W. Colquhoun H.M. Daniels J.A. Stephenson I.R. Wade K. *J. Chem. Soc. Chem. Comm.* 1987 889-891
2. Porterfield W.W. Stephenson I.R. Wade K. "Boron Chemistry" Proceedings of the 6th International Meeting (Ed. Hermanek S.) World Scientific Singapore 1987 p3-25

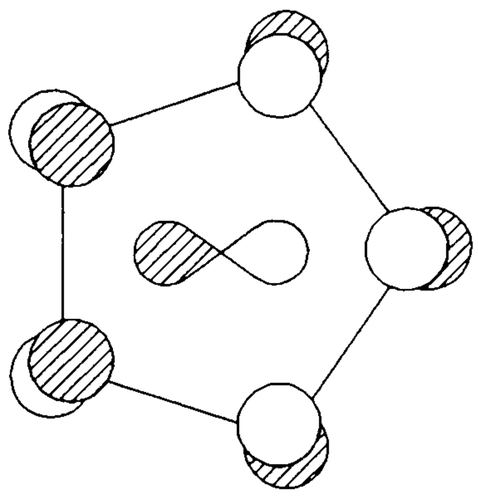


Molecular orbital rationalization of the way a CO unit can interact with a *nido*-shaped CB_{10} residue has been made; the orbitals involved in bonding the carbonyl carbon atom to the rest of the carborane icosahedron are shown below[1]. The $6a_1$ orbital functions as the one into which the lone pair electrons on the carbon of the carbonyl group are formally donated. Back π-bonding occurs from the orbitals $5e_1(x)$ and $5e_1(y)$ to the π^* orbitals of the carbonyl group. Because of the interesting structure of the anion, certain other carborane derivatives were targeted to give possible products of deprotonation whose structures and electron densities could be investigated by X-ray and n.m.r. studies.

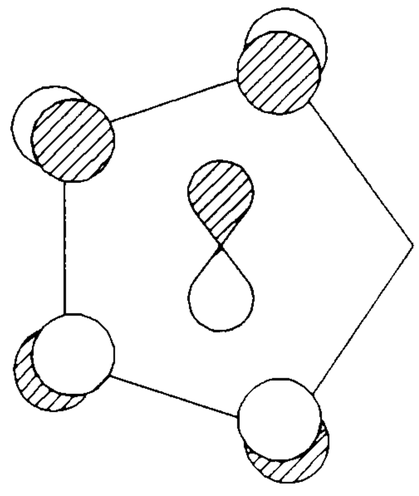




$6a_1$

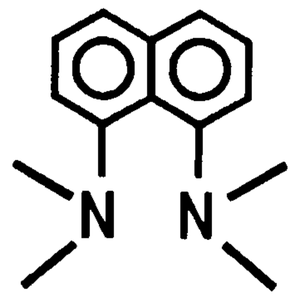


$5e_1(x)$



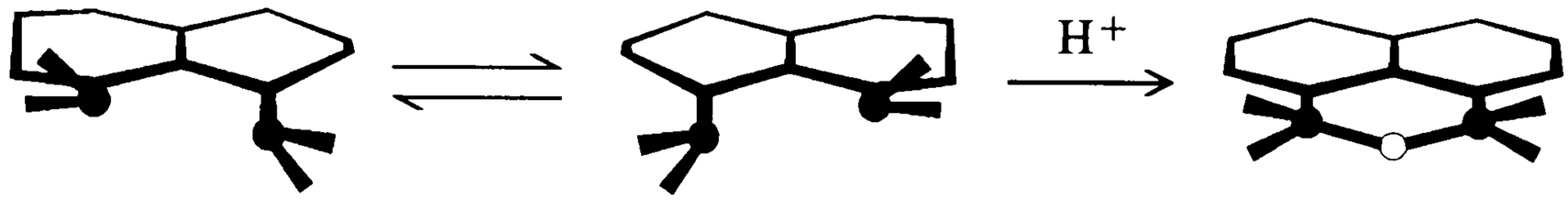
$5e_1(y)$

N,N,N′,N′-tetramethyl-1,8-diaminonaphthalene (**II**), also known as proton sponge, is a strong base with a pK_a value of 12.34 in water[3]. The remarkable basicity is due to the strained conformation of the proton sponge caused by steric hindrance preventing resonance interactions between the dimethylamino groups and the rings whereas the cation formed on addition of a proton has a less strained conformation[4,5].



II

● N ○H



II **II**

This chapter contains six parts, each of different types of carborane derivatives. They are carbon-hydroxy, carbon-sulphur, carbon-diaryl, boron-decachloro, boron-hydroxy and carbon-amino carboranes.

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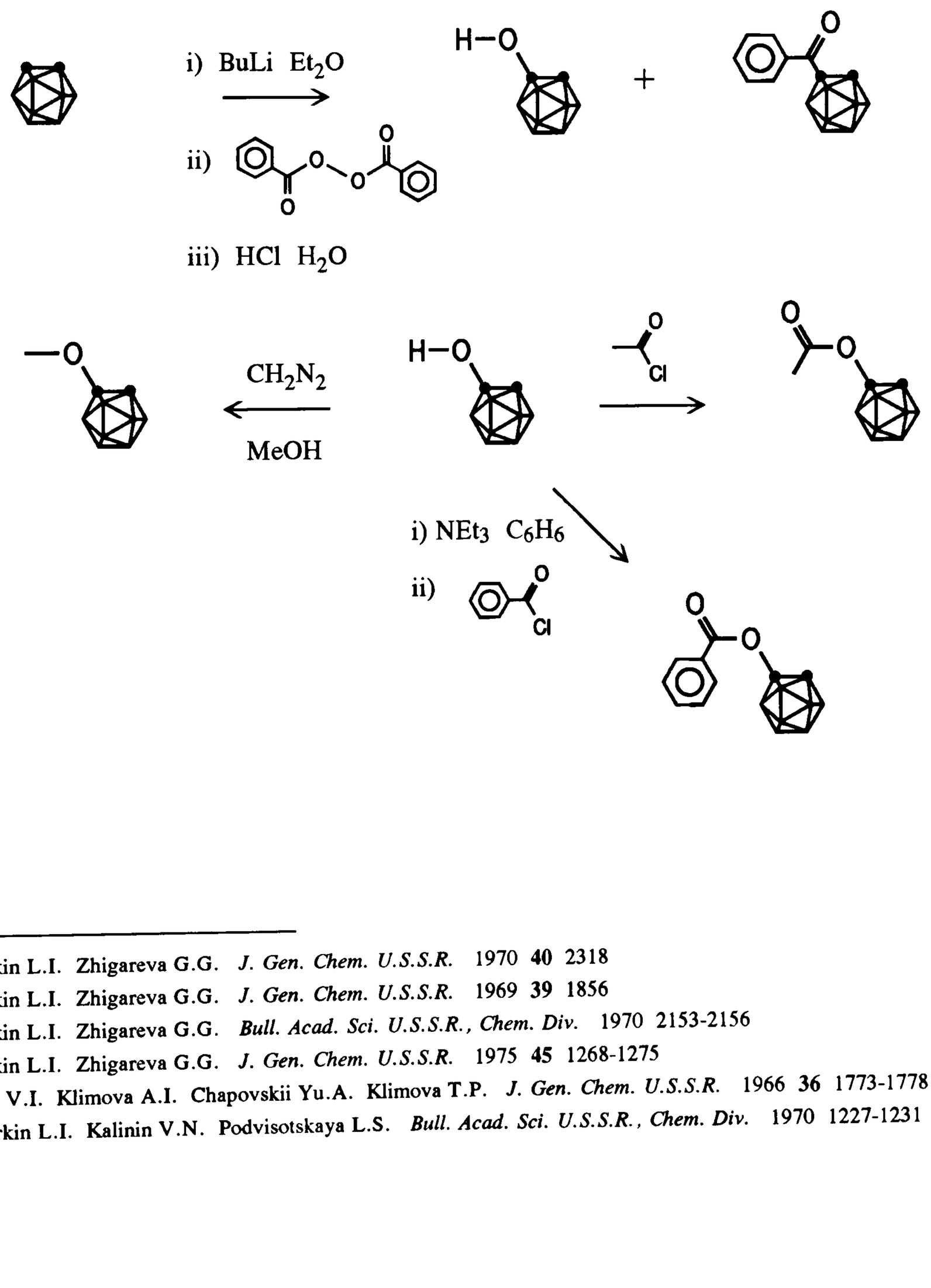
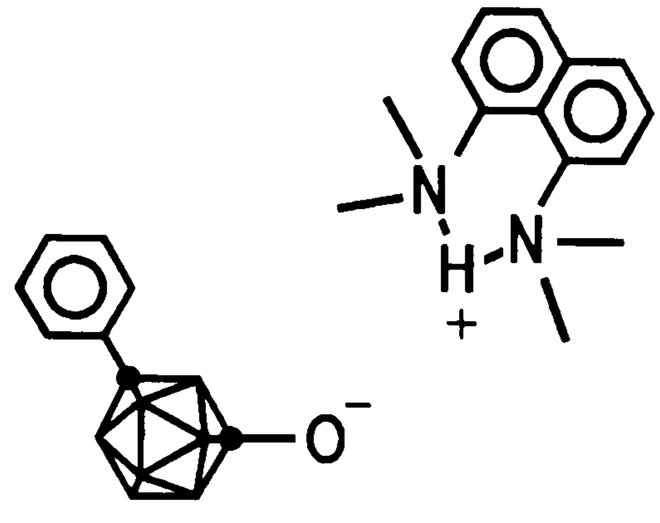
3. Alder R.W. Bowman P.S. Steele W.R.S. Winterman D.R. *Chem. Commun.* 1968 723-724
4. Alder R.W. Anderson J.E. *J. Chem. Soc. Perkin II* 1973 2086-2088
5. Einspahr H. Robert J.B. Marsh R.E. Roberts J.D. *Acta Cryst.* 1973 **B29** 1611-1617

CARBON-HYDROXY CARBORANES

Carbon-hydroxy carboranes can be formed from parent carboranes by reaction of their lithium derivatives with oxygen[6] or benzoyl peroxide[7,8]. They can also be obtained from carbon-amino carboranes and nitrosyl hydrogen sulphate[9]. The benzoyl peroxide reaction gives the best yield of carbon-hydroxy carboranes from parent carboranes according to the literature. The unwanted products, carbon-benzoyl carboranes, can easily be reconverted into the starting carboranes with weak alkali[10,11]. Carbon-hydroxy carboranes, like phenols, react with acetyl chloride, benzoyl chloride and diazomethane to give carbon-acetoxy, carbon-benzoxy and carbon-methoxy carboranes respectively[8].

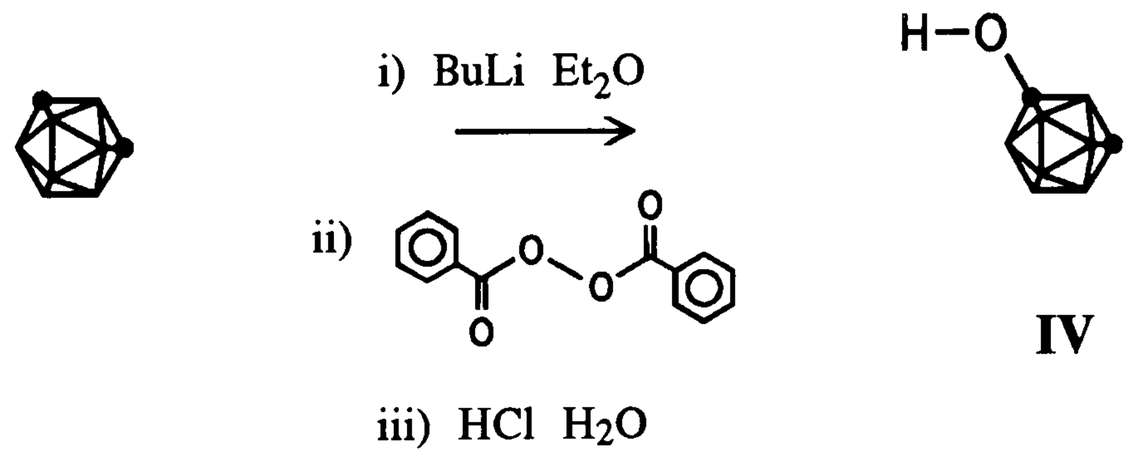


6. Zakharkin L.I. Zhigareva G.G. *J. Gen. Chem. U.S.S.R.* 1970 **40** 2318
7. Zakharkin L.I. Zhigareva G.G. *J. Gen. Chem. U.S.S.R.* 1969 **39** 1856
8. Zakharkin L.I. Zhigareva G.G. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1970 2153-2156
9. Zakharkin L.I. Zhigareva G.G. *J. Gen. Chem. U.S.S.R.* 1975 **45** 1268-1275
10. Stanko V.I. Klimova A.I. Chapovskii Yu.A. Klimova T.P. *J. Gen. Chem. U.S.S.R.* 1966 **36** 1773-1778
11. Zakharkin L.I. Kalinin V.N. Podvisotskaya L.S. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1970 1227-1231

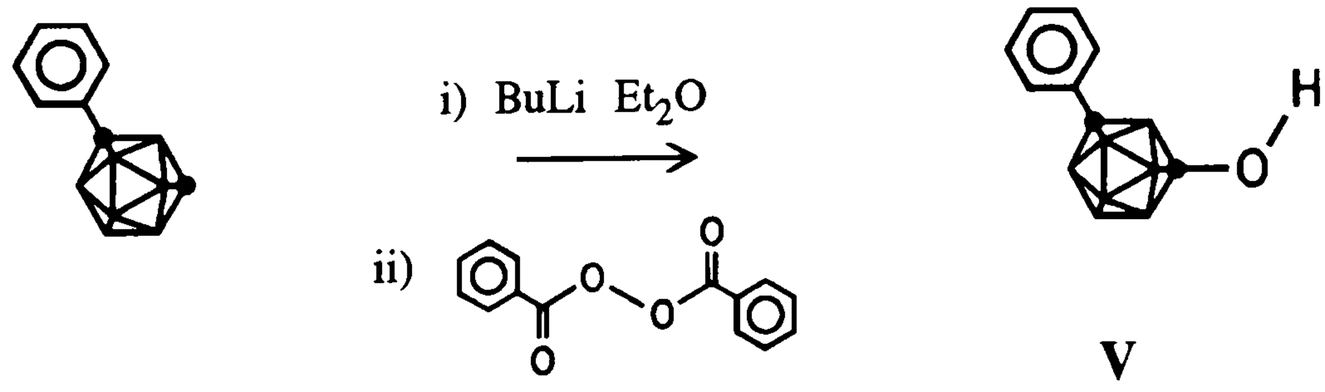


III

The product of deprotonation of 1-phenyl-7-hydroxy-*meta*-carborane (**III**) was targeted as the anion could contain a *nido*-shaped $PhCB_{10}H_{10}^-$ residue with a B_5 open face capped by a pentuply-bridging carbonyl group. 1-hydroxy-*meta*-carborane (**IV**) was successfully obtained from 1-lithio-*meta*-carborane and benzoyl peroxide. The same method was carried out on 1-phenyl-*meta*-carborane to produce 1-phenyl-7-hydroxy-*meta*-carborane (**V**) in good yield. However 1-phenyl-7-hydroxy-*meta*-carborane did not produce the expected 1:1 adduct with proton sponge, an adduct of approximately 4:1 carborane : proton sponge was obtained. The 4:1 ratio is difficult to understand as a salt would require equimolar proportions of carborane and proton sponge.

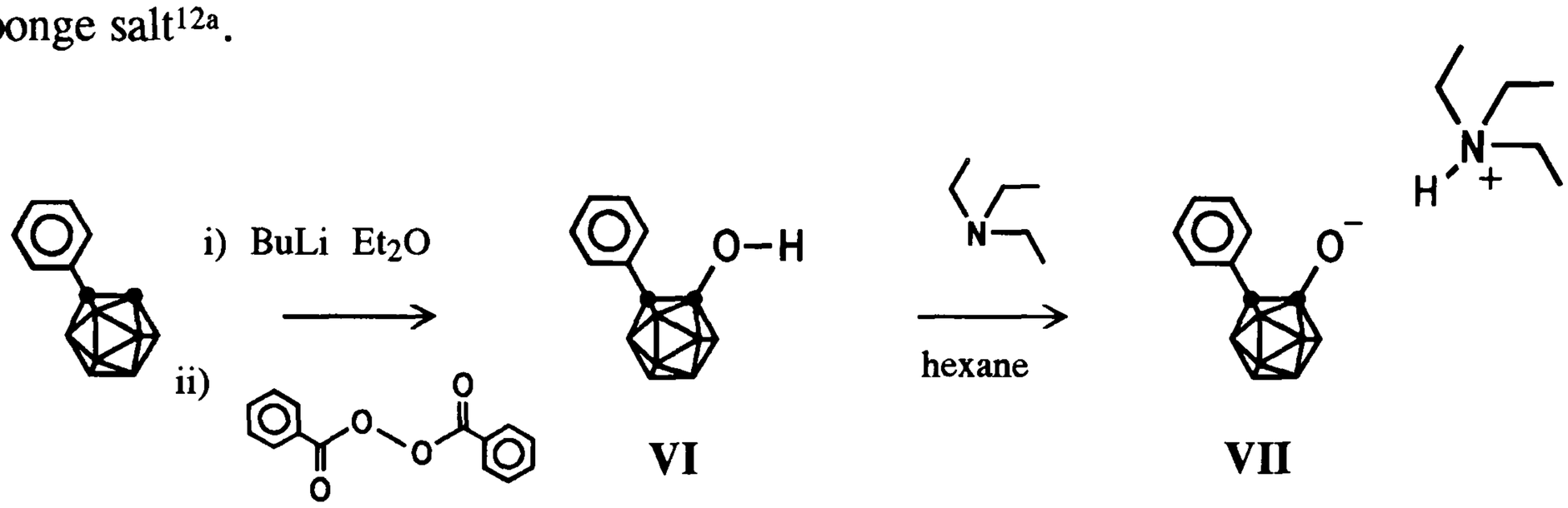


IV

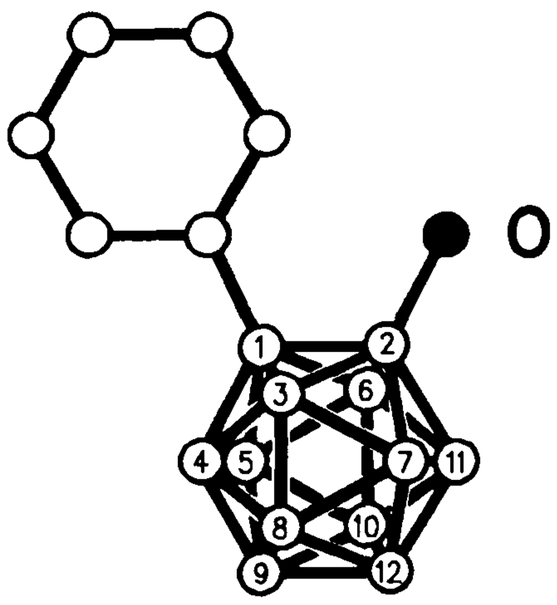


V

1-phenyl-2-hydroxy-*ortho*-carborane (**VI**) was made in order to observe the 3700-3000cm^{-1} region of its infra red spectrum and to obtain ^{13}C n.m.r. data of the triethylamine adduct (**VII**). The four bands which are approximately 150cm^{-1} apart at 3600-3000cm^{-1} suggest that the hydroxy compound is a hydrate but curiously other characterization data do not indicate any water molecules present. An explanation for this phenomenon could be that hydrogen bonding exists in the solid state of this compound. The ^{13}C n.m.r. data for the triethylamine adduct of 1-phenyl-2-hydroxy-*ortho*-carborane indicate that the adduct is of high ionic character by comparison with ^{13}C n.m.r. data of the proton sponge salt[12a].



Comparisons of carboranyl ^{13}C n.m.r. peaks of 1-phenyl-2-hydroxy-*ortho*-carborane (**VI**) and salts (**VII** and **I**)

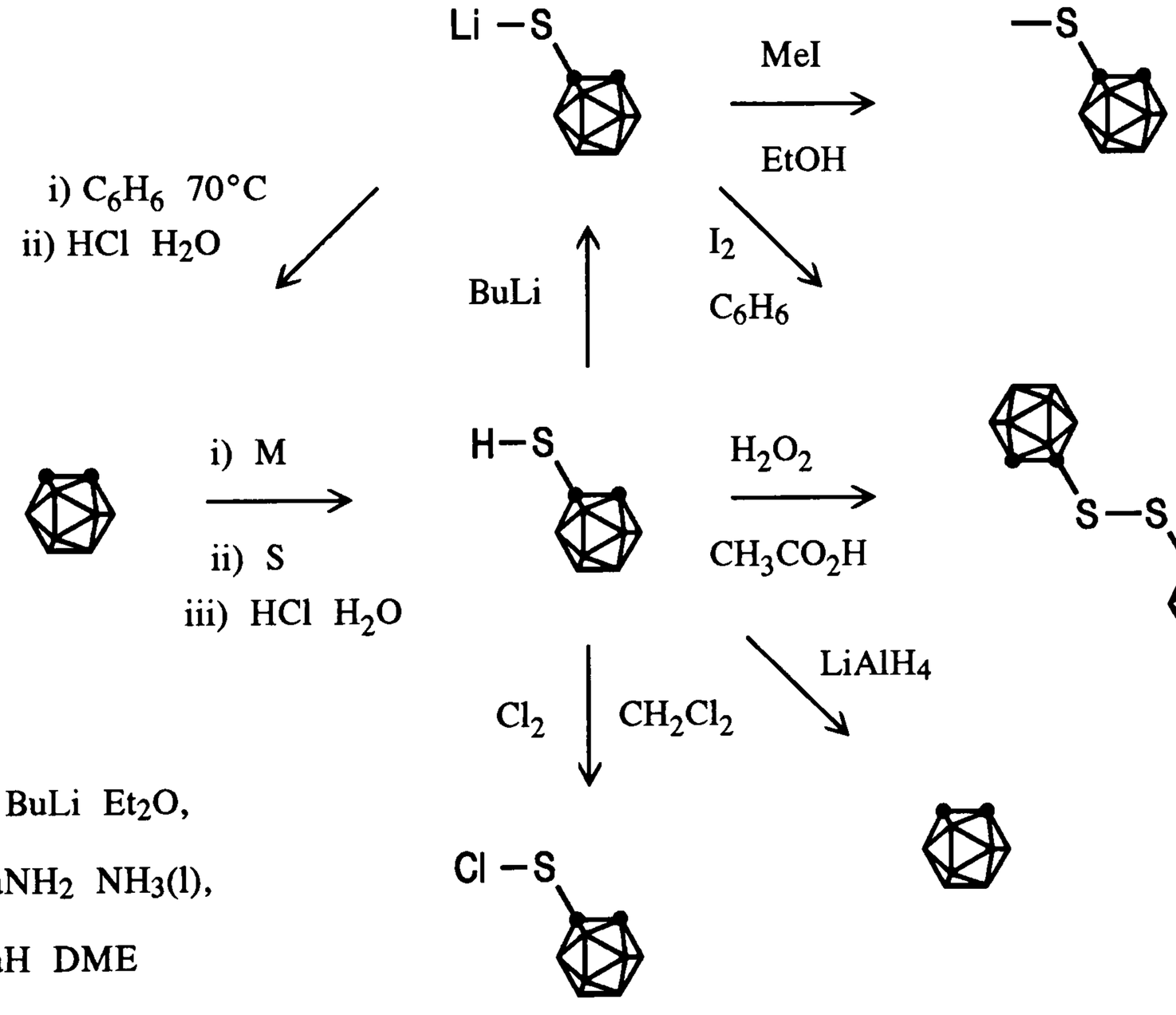


compound	C(1)	C(2)	solvent
VI	90.51	102.70	$CDCl_3$
VII	88.52	129.92	$CDCl_3$
I	88.12	136.42	$(CD_3)_2CO$

12. Stephenson I.R. "Novel Polymer and Derivative Chemistry of Icosahedral Carboranes" Ph.D. Thesis University of Durham Durham 1988 a) p176 b) p173 c) p174

CARBON-MERCAPTO CARBORANES

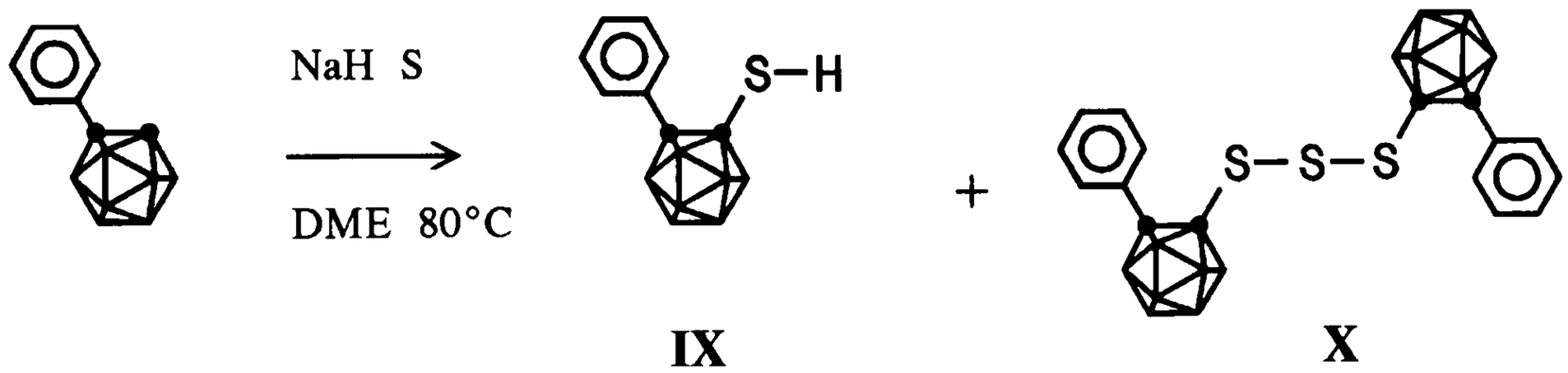
Carbon-mercapto carboranes are produced through reaction of alkali metal or magnesium derivatives of parent carboranes with sulphur powder followed by hydrolysis[13,14,15,16,17,18]. The thiols react with hydrogen peroxide in acetic acid to produce disulphides and sulphonic acids and chlorine in methylene chloride to give sulphenyl halides[18]. Alkali metal derivatives of the carbon-mercapto carboranes give carborane methyl sulphides with methyl iodide and carborane disulphides with iodine[16,18]. The thiols can be reconverted into their starting carboranes by reaction with lithium aluminium hydride[19] or with *neo*-butyllithium at 70°C[18].



Formation and reactions of 1-mercapto-*ortho*-carborane

13. Plesek J. Hermanek S. *Coll. Czech. Chem. Comm.* 1981 **46** 687-692
14. Zakharkin L.I. Kalinin V.N. Zhigareva G.G. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1970 857-859
15. Zakharkin L.I. Zhigareva G.G. Kazantsev A.V. *J. Gen. Chem. U.S.S.R.* 1968 **38** 86-89
16. Zakharkin L.I. Zhigareva G.G. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1967 1308-1310
17. Smith H.D.Jr. Obenland C.O. Papetti S. *Inorg. Chem.* 1966 **3** 1013-1015
18. Zakharkin L.I. Zhigareva G.G. *J. Gen. Chem. U.S.S.R.* 1975 **45** 777-785
19. Zakharkin L.I. Zhigareva G.G. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1969 546-550

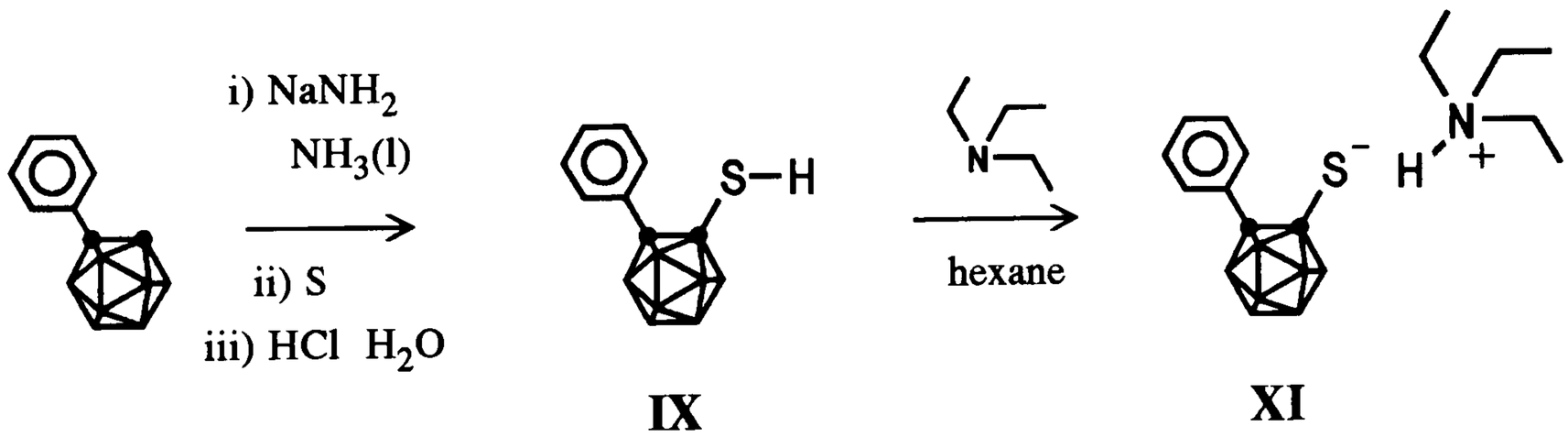
The product of deprotonation of 1-phenyl-2-mercapto-*ortho*-carborane (**VIII**) was expected to give similar cage distortions to the oxygen analogue. The sodium hydride method was attempted on 1-phenyl-*ortho*-carborane which gave low yields of the expected product 1-phenyl-2-mercapto-*ortho*-carborane (**IX**) and a novel product found by X-ray studies to be 2,2′-bis(1-phenyl-*ortho*-carboranyl) trisulphide (**X**). 1-phenyl-2-mercapto-*ortho*-carborane was also obtained in good yield from 1-phenyl-*ortho*-carborane using sodium amide and sulphur in liquid ammonia. The thiol was then treated with proton sponge to give a salt where its structure was determined by X-ray crystallography.



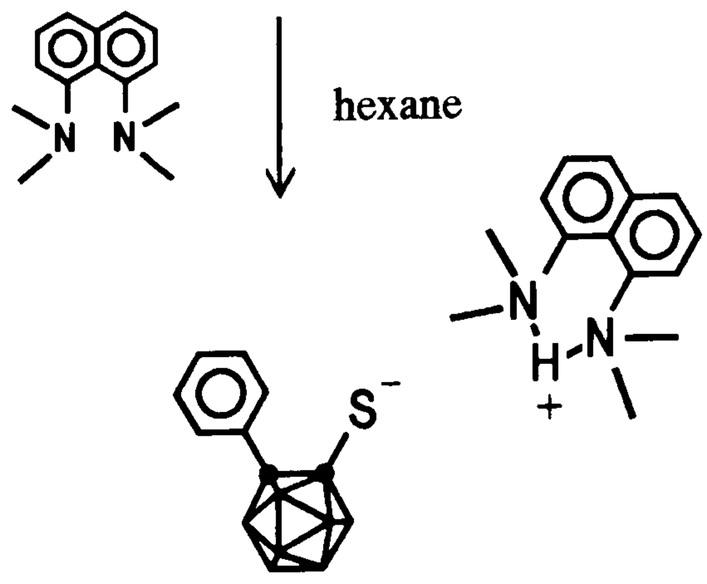
IX 16%

X 4%

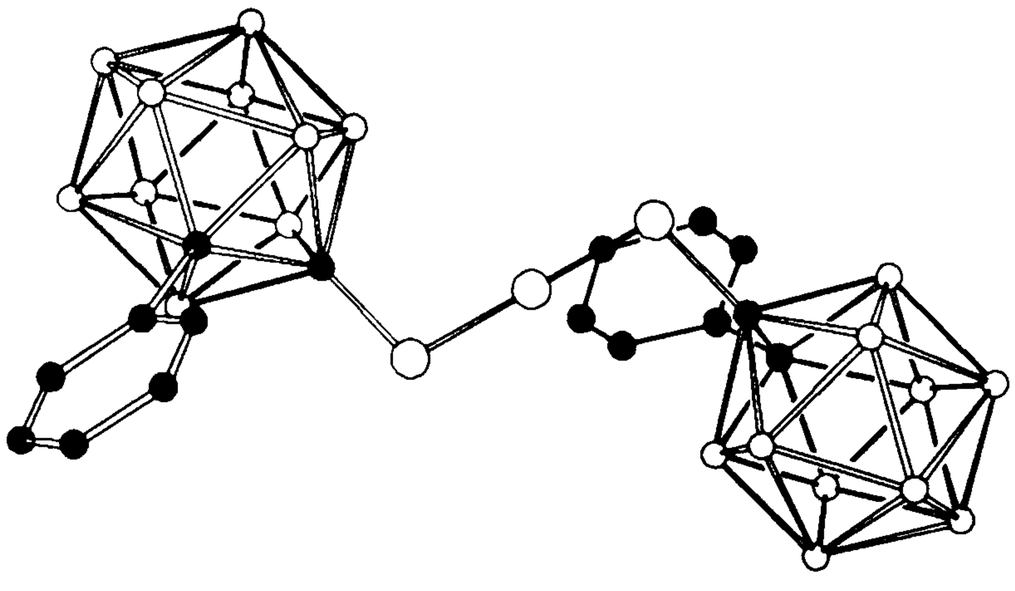
DME = 1,2-dimethoxyethane



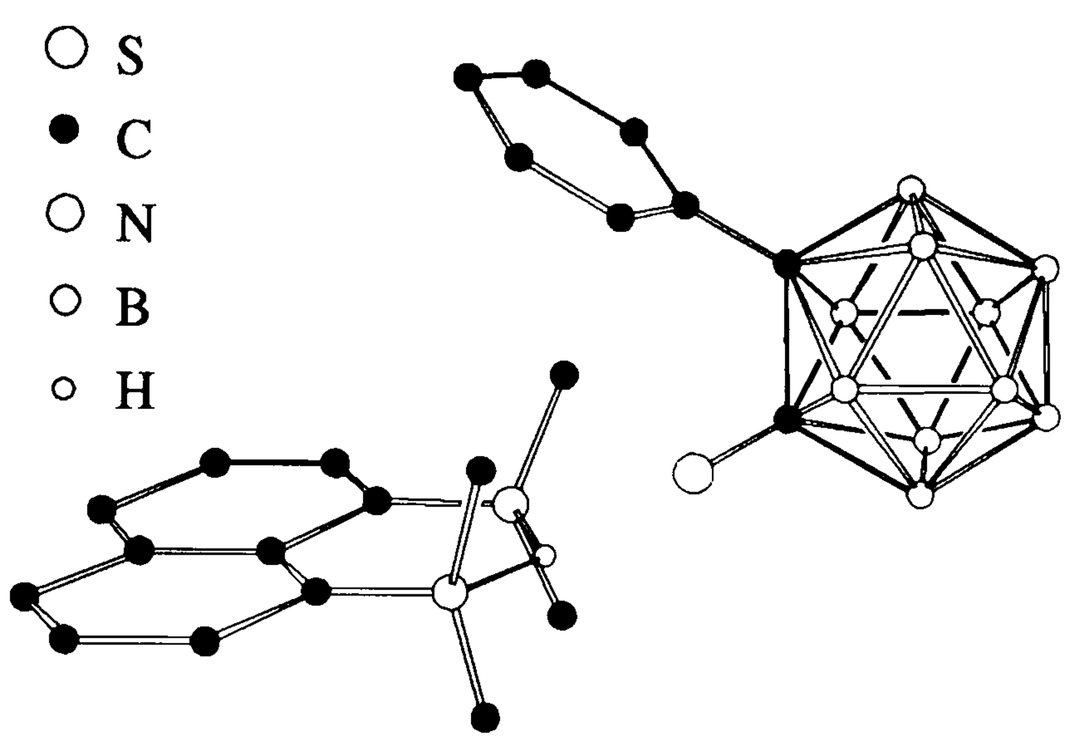
IX **XI**



VIII

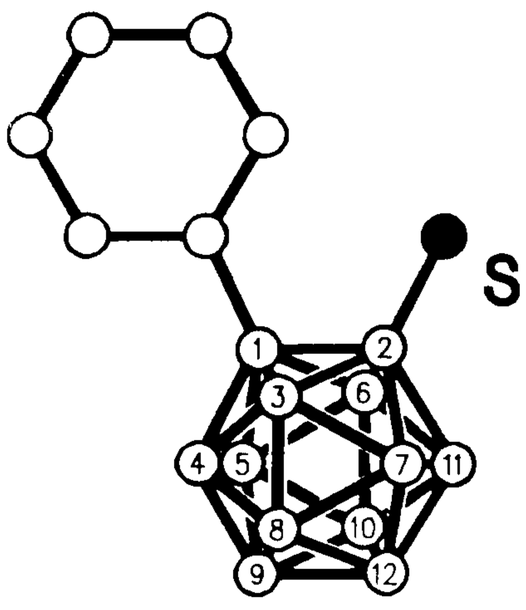


X-ray structure of **X**, $PhCB_{10}H_{10}CS_3CB_{10}H_{10}CPh$

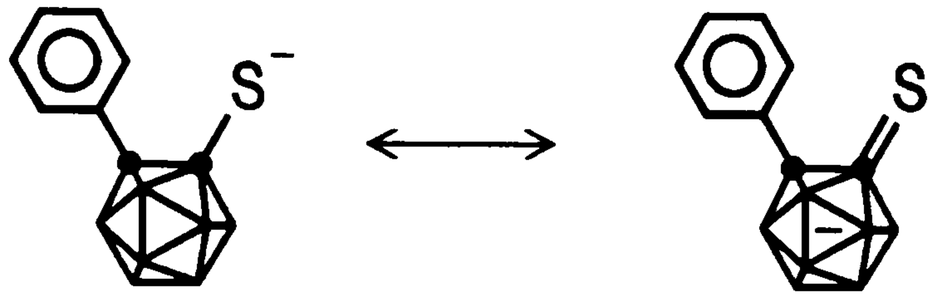


X-ray structure of **VIII**, $[PhCB_{10}H_{10}CS]^-[C_{10}H_6(NMe_2)_2H]^+$

Comparisons of selected bond lengths and angle of **X** and **VIII**



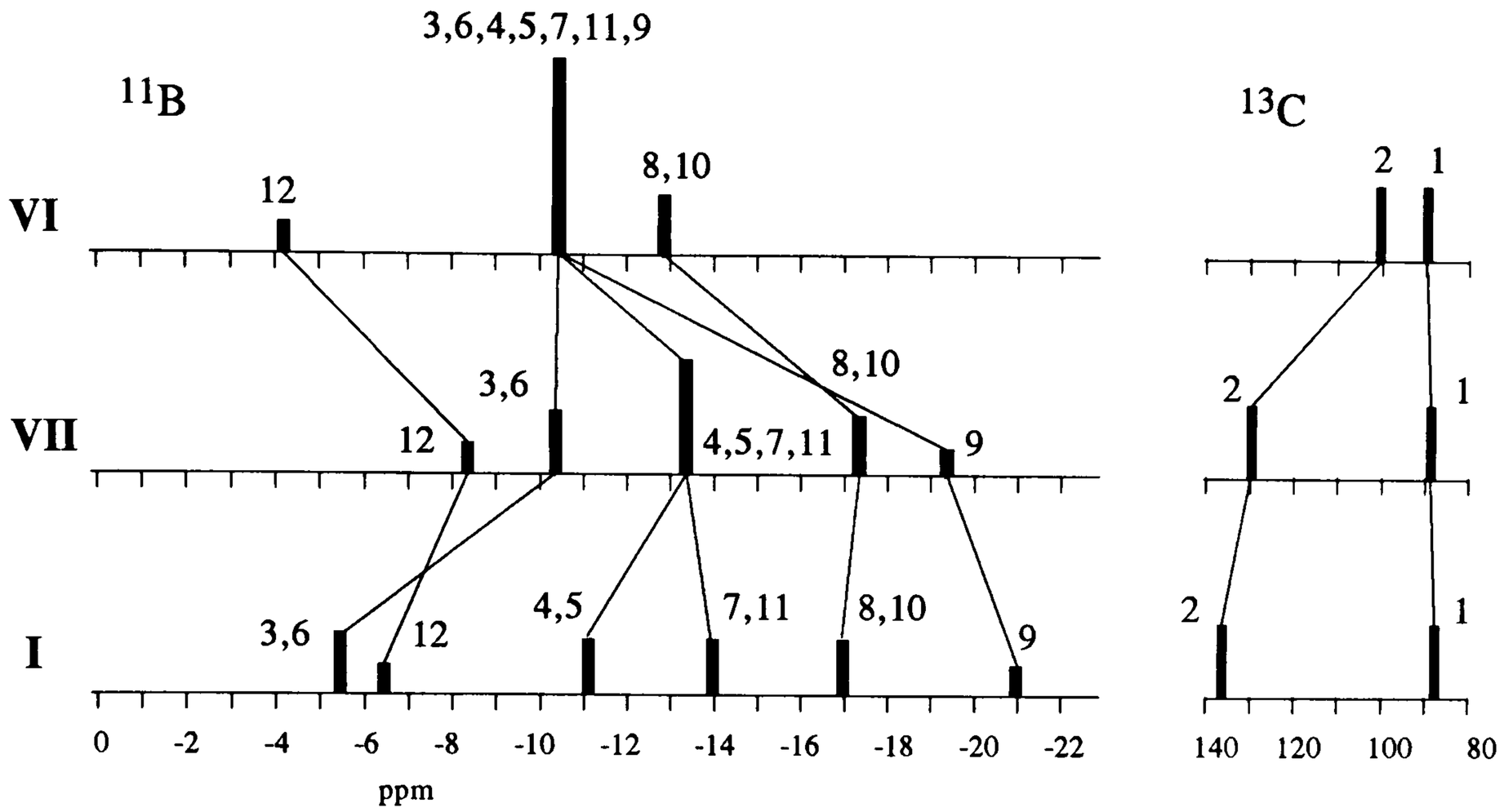
Bond length (Å)	**X**	**VIII**
C(2)-S	1.791	1.729
C(1)-C(2)	1.729	1.835
B(3)-C(2)	1.726	1.749
B(6)-C(2)	1.711	1.742
B(7)-C(2)	1.708	1.704
B(11)-C(2)	1.695	1.695
Bond angle (°)	**X**	**VIII**
S-C(2)-C(1)	115.8	119.8



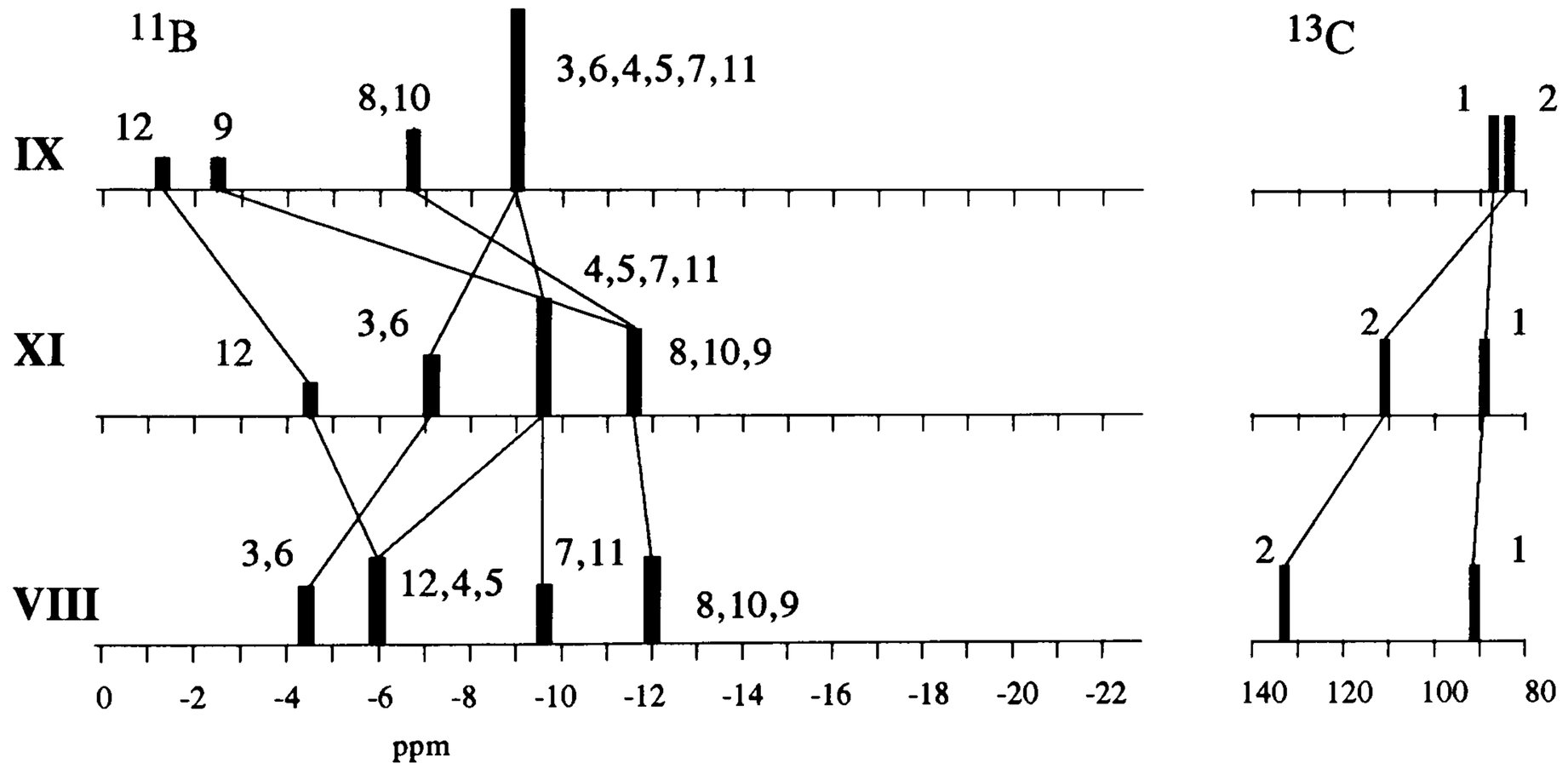
The structure of 1-phenyl-2-thio-*ortho*-carborane anion, $PhCB_{10}H_{10}CS^-$, reveals the expected pentuply-bridging environment of the CS group and shows that the methyl groups of the base effectively prevent N-H···S hydrogen bonding between the cation and anion. Evidence for delocalization of the anionic charge from the sulphur atom into the carborane cage is provided by the carbon-sulphur bond length which, at 1.73Å, is shorter than 1.79Å found in the trisulphide. Interestingly, although within the *nido*-$PhCB_{10}H_{10}^-$ residue the cage C-B and B-B distances lie in the range (1.69Å - 1.79Å) usual for such icosahedral fragments, the C-C and C-B bonds to the CS unit have lengths that show the CS unit to be shifted significantly away from the other carboranyl carbon. This anion structure is similar to the anion structure in the proton sponge salt of 1-phenyl-2-hydroxy-*ortho*-carborane.

Comparing the ^{13}C n.m.r. spectrum of 1-phenyl-2-thio-*ortho*-carborane anion and of 1-phenyl-2-mercapto-*ortho*-carborane (simplified spectra overleaf), a significant deshielding of 48ppm is observed in the C(2) peak. In the ^{11}B n.m.r. spectra of these carboranes, the B(9) peak is shielded by 10.5ppm due to the antipodal effect while the changes in the other boron peaks are not as obvious. The trends of the carboranyl ^{13}C and ^{11}B peaks of the thiol and its deprotonated form are very similar to those observed for the oxygen analogues.

By X-ray and n.m.r. studies it is deduced that the structure and electron delocalization are similar in 1-phenyl-2-thio-*ortho*-carborane anion and 1-phenyl-2-oxo-*ortho*-carborane anion. Thus the molecular orbital rationalization of the way a CS unit can interact with the *nido*-$PhCB_{10}H_{10}^-$ residue of the sulphur-containing anion is identical to the rationalization made for the oxygen analogue (orbital diagrams are shown on page 258).

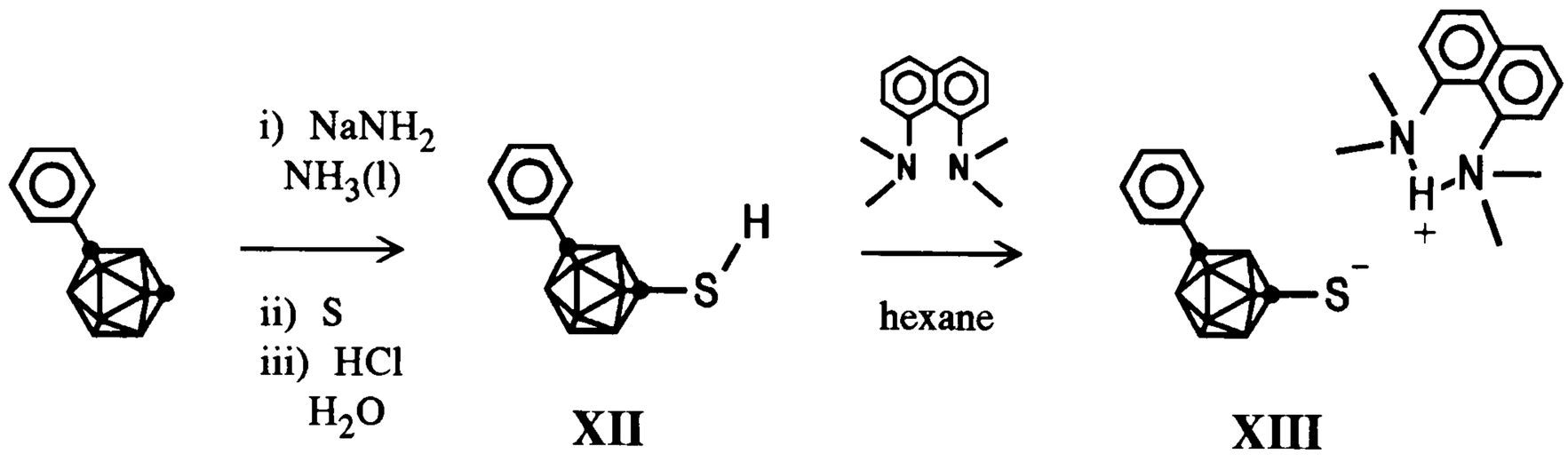


Carboranyl NMR peaks of 1-phenyl-2-hydroxy-*ortho*-carborane (**VI**) and salts (**VII** and **I**) above and 1-phenyl-2-mercapto-*ortho*-carborane (**IX**) and salts (**XI** and **VIII**) below.



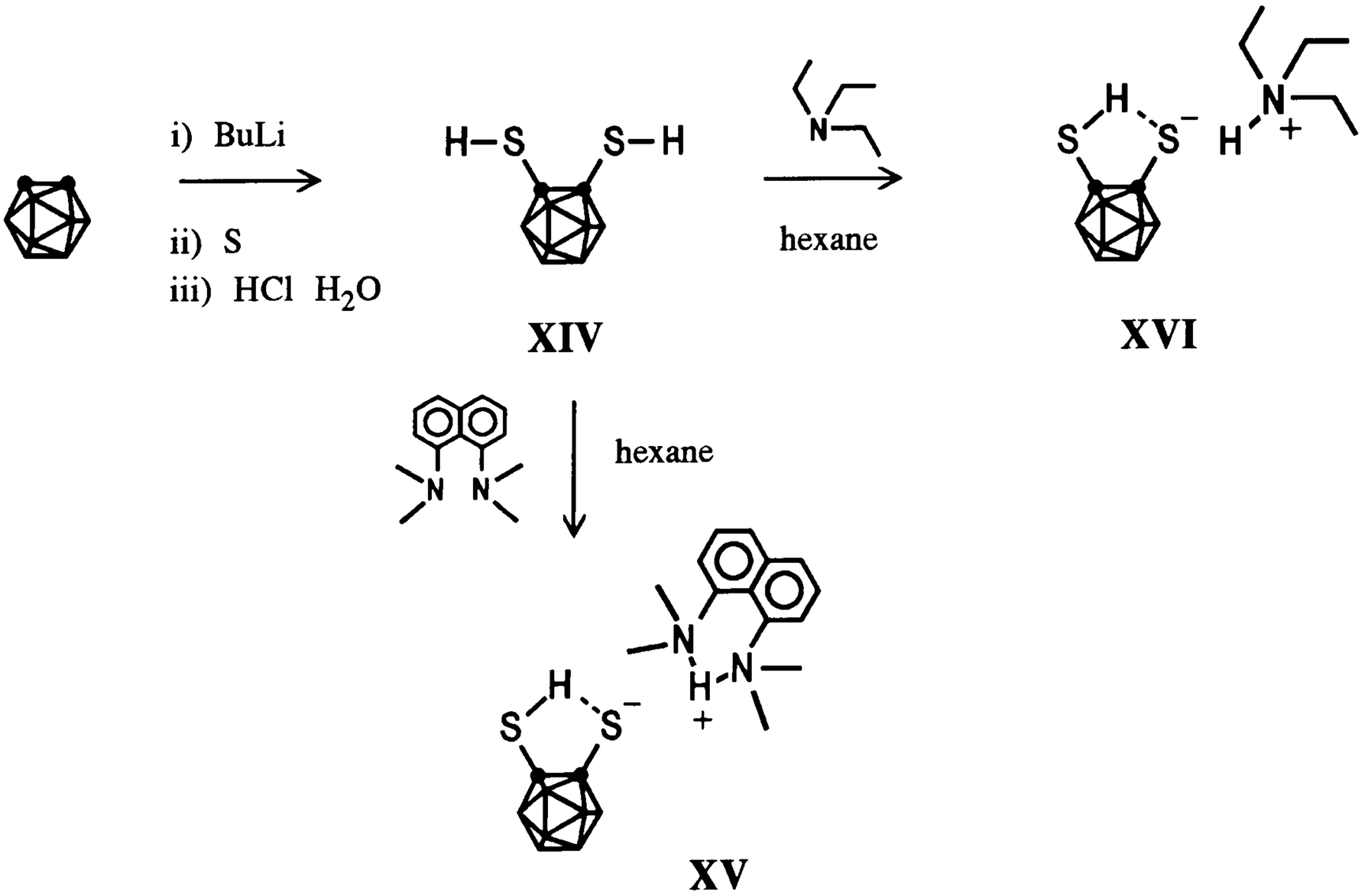
1-phenyl-7-mercapto-*meta*-carborane (**XII**) was also produced in good yield by the sodium amide method. A 1:1 proton sponge : 1-phenyl-7-mercapto-*meta*-carborane adduct (**XIII**) was obtained from the thiol and proton sponge in hexane. The powdered adduct was insoluble in known solvents so unfortunately solution state n.m.r. and X-ray studies could not be carried out on this adduct. 1-phenyl-7-mercapto-*meta*-carborane must be more acidic than 1-phenyl-7-hydroxy-*meta*-carborane as a 1:1 adduct could be precipitated with proton sponge from the former only. This agrees with the pK_a values (in 50% ethanol) found in

similar derivatives, 1-hydroxy-*meta*-carborane has a value of 8.24[8] whereas 1-mercapto-*meta*-carborane has 5.30[13].



XII **XIII**

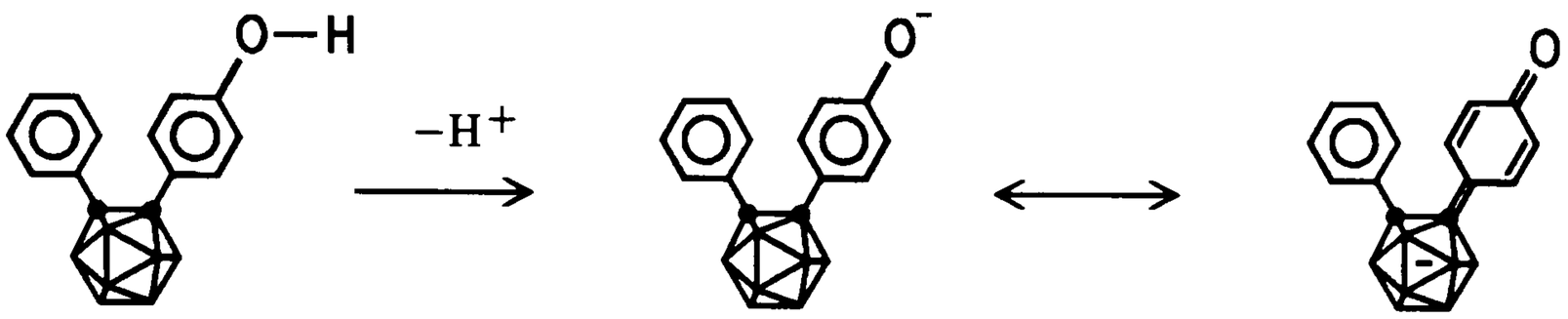
1,2-dimercapto-*ortho*-carborane (**XIV**) was investigated for the possibility of a 2:1 proton sponge : 1,2-dimercapto-*ortho*-carborane salt which could have an interesting cage structure. The dithiol was produced from 1,2-dilithio-*ortho*-carborane and powdered sulphur followed by hydrolysis. 1,2-dimercapto-*ortho*-carborane gave a 1:1 salt with proton sponge (**XV**) and ^{13}C solid state n.m.r. data of this salt showed equivalent carboranyl carbons. Crystals of this salt gave only weak reflections on X-ray diffraction so its molecular structure could not be determined. A 1:1 triethylamine : 1,2-dimercapto-*ortho*-carborane adduct (**XVI**) was also produced and its anion is expected to be similar to the anion in the proton sponge : dithiol salt according to its ^{11}B and ^{13}C n.m.r. data.



XIV **XVI**

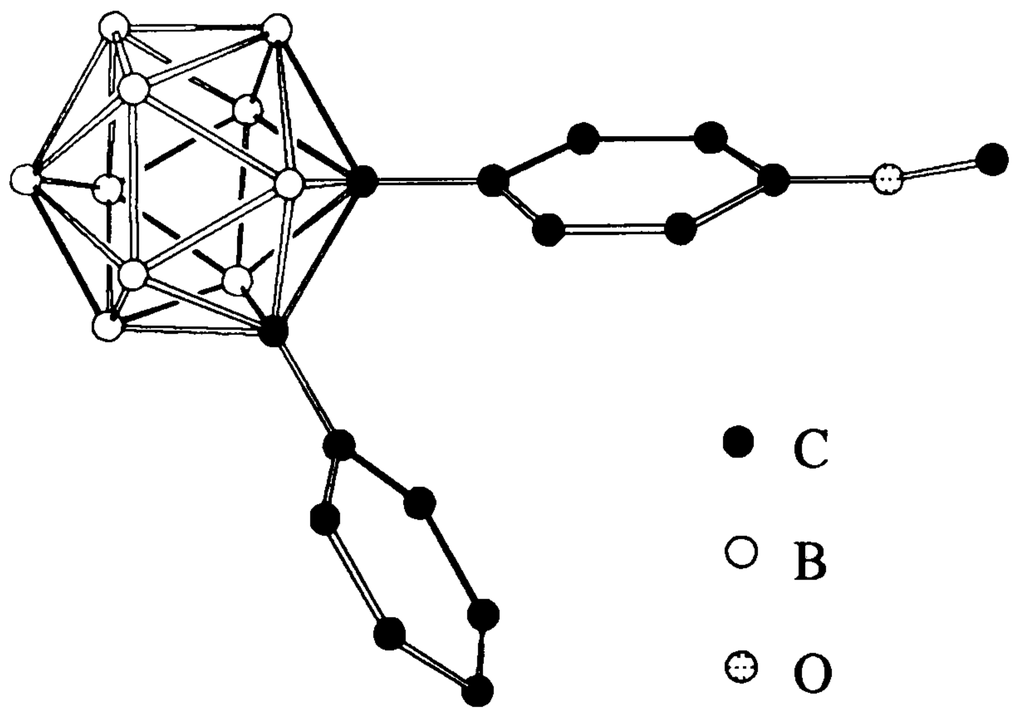
XV

DIARYL CARBORANES



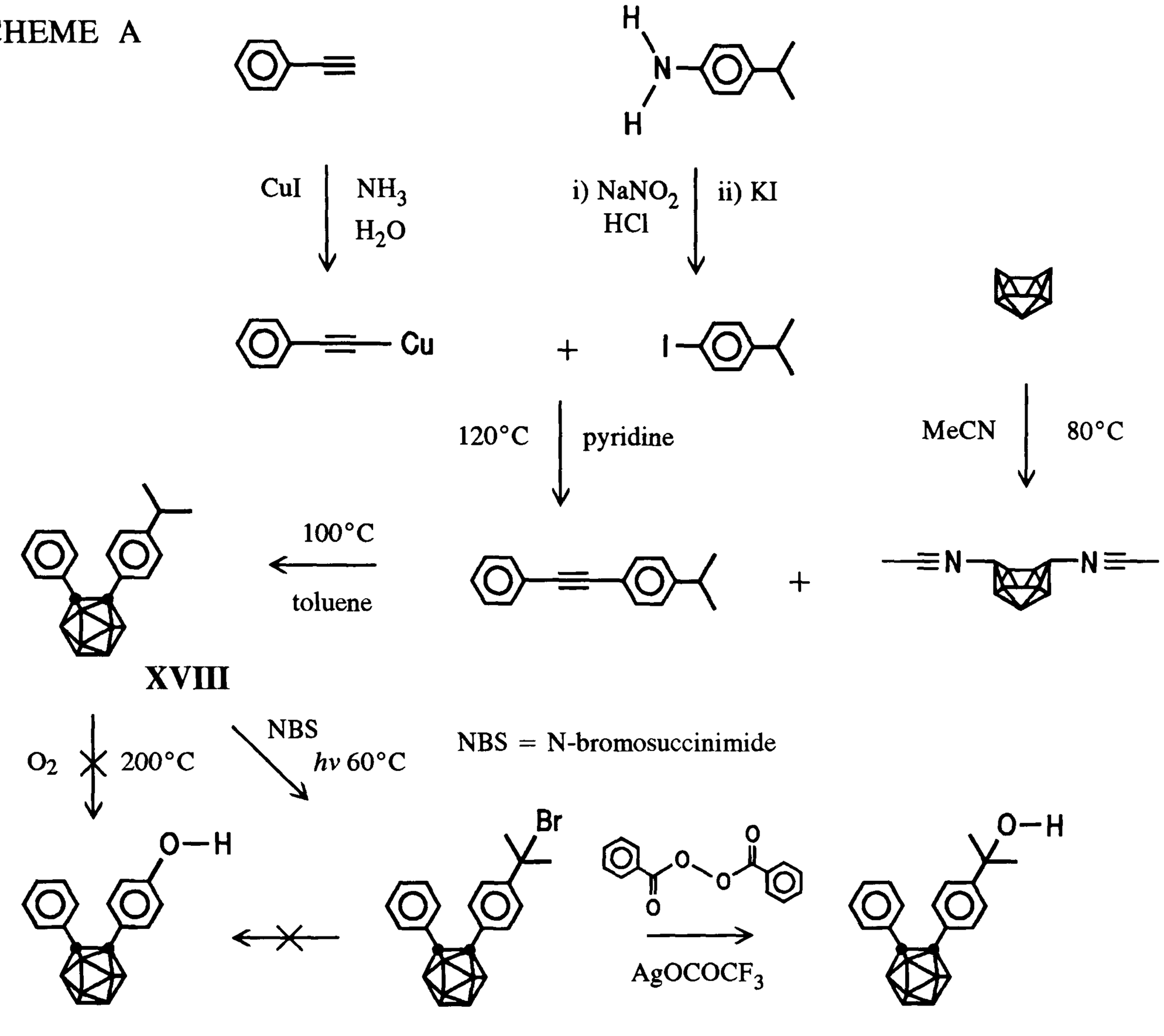
XVII

1-phenyl-2-(4-hydroxyphenyl)-*ortho*-carborane (**XVII**) could in principle be deprotonated to induce π-bonding between the ring and cage so this diaryl derivative was targeted by the three schemes A, B and C. They were based on common preparations of phenols but only the last scheme, C, gave the target compound. The hydroxy compound was treated with proton sponge in hexane but the solution gave no precipitate and ^{11}B n.m.r. spectroscopy of the solution showed peaks identical to the starting carborane. Hexane was removed from the solution under vacuum to leave a residue containing starting materials as indicated by infrared and solution-state ^{13}C n.m.r. spectroscopy. An X-ray study has been carried out on 1-phenyl-2-(4-methoxyphenyl)-*ortho*-carborane (**XXIII**) to be used as a reference for comparison if the anion of the hydroxy carborane can be prepared and structurally characterized.



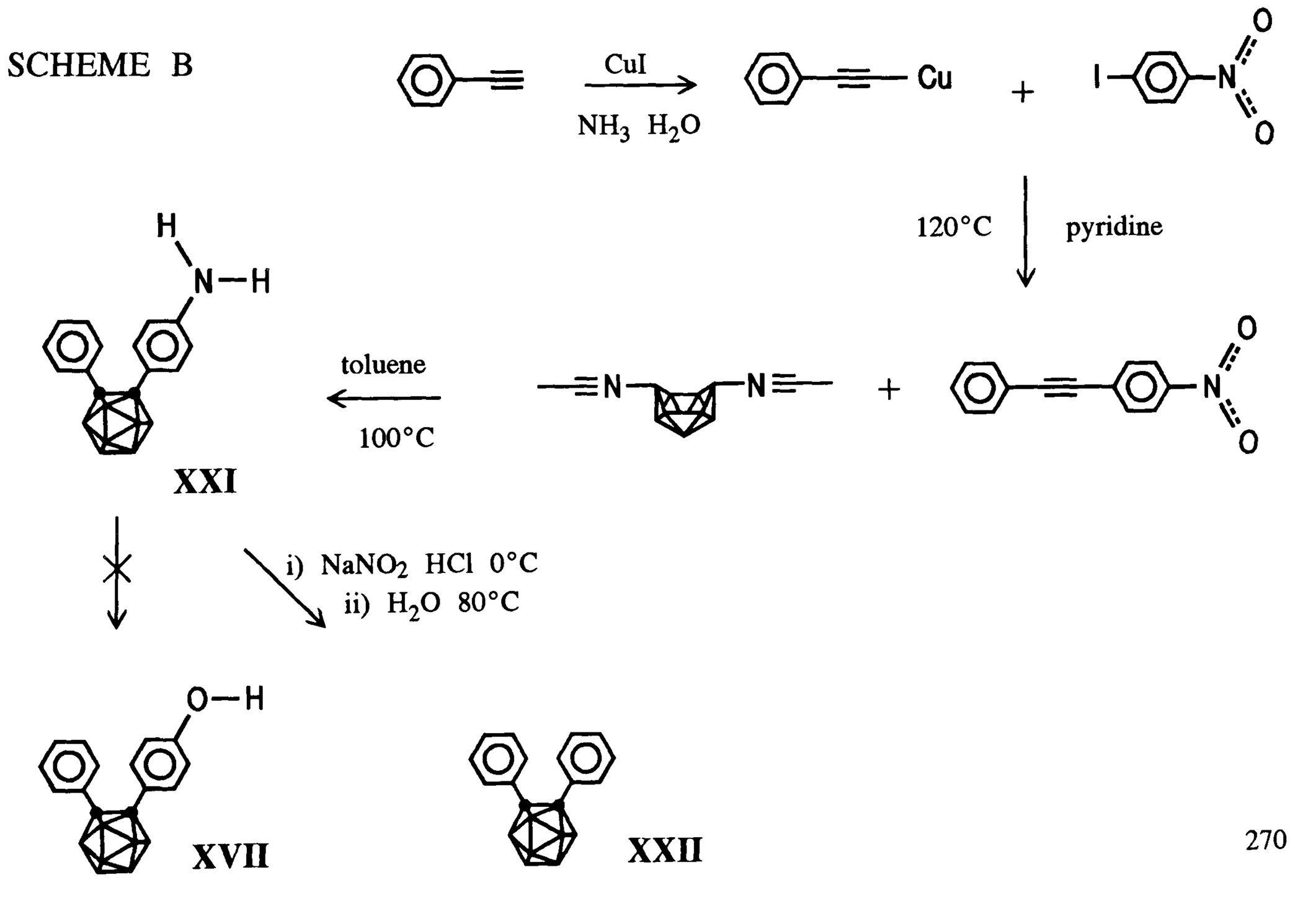
X-ray structure of **XXIII**

SCHEME A



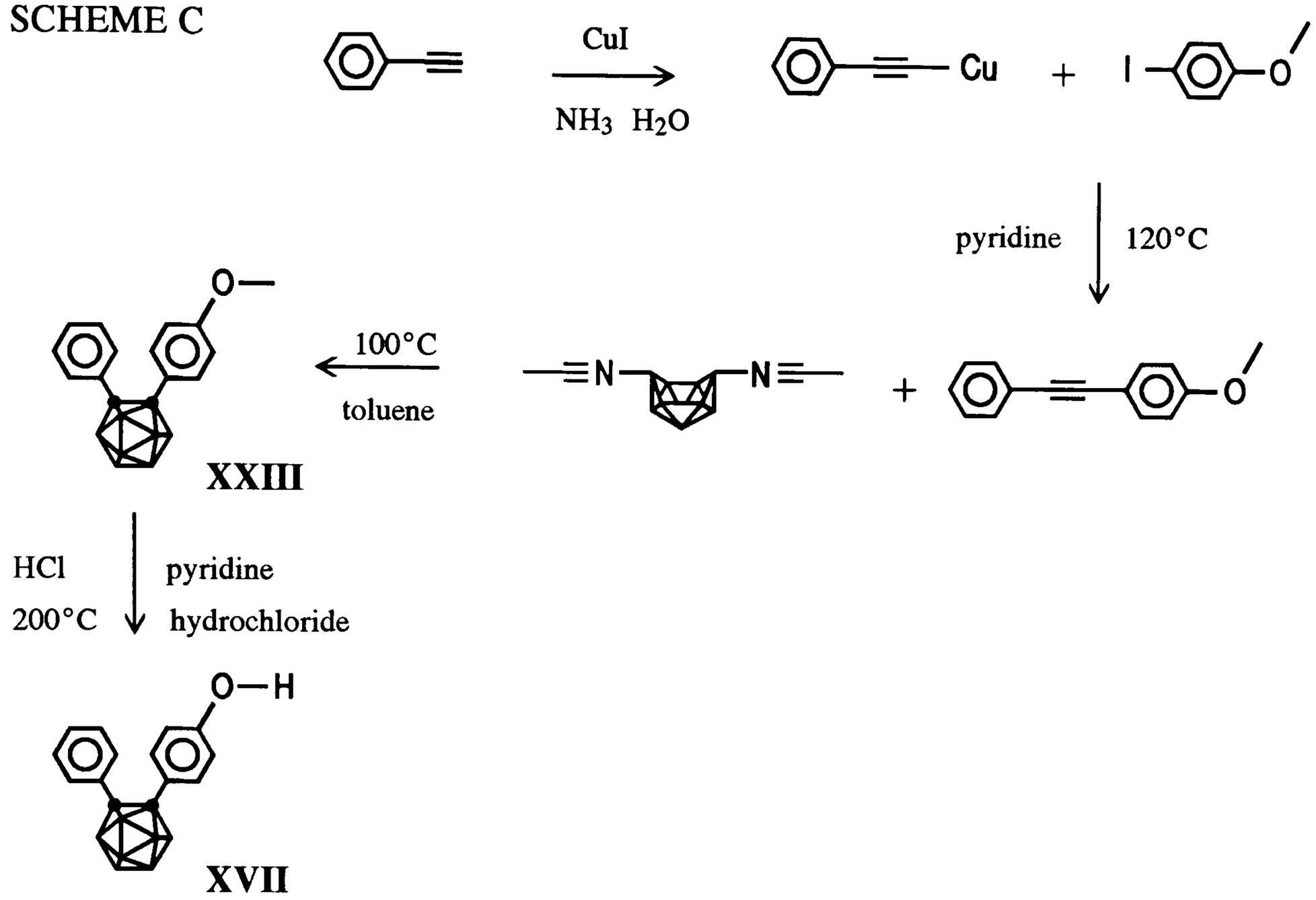
XVII **XVIII** **XIX** **XX**

SCHEME B



XXI **XVII** **XXII**

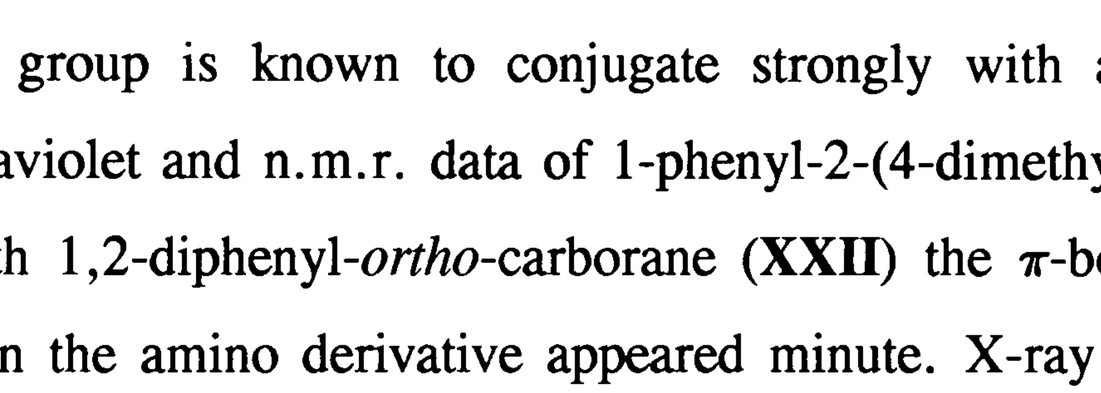
SCHEME C



XXIII

XVII

1-phenyl-2-(4-dimethylaminophenyl)-*ortho*-carborane (**XXIV**) was also made (Scheme D) to observe possible π-bonding between the ring and cage as the dimethylamino group is known to conjugate strongly with aryl π-systems. Comparing the ultraviolet and n.m.r. data of 1-phenyl-2-(4-dimethylaminophenyl)-*ortho*-carborane with 1,2-diphenyl-*ortho*-carborane (**XXII**) the π-bonding between the ring and cage in the amino derivative appeared minute. X-ray analysis of the compound is needed for molecular structure determination before making conclusive deductions about ring-cage π-bonding in this compound.

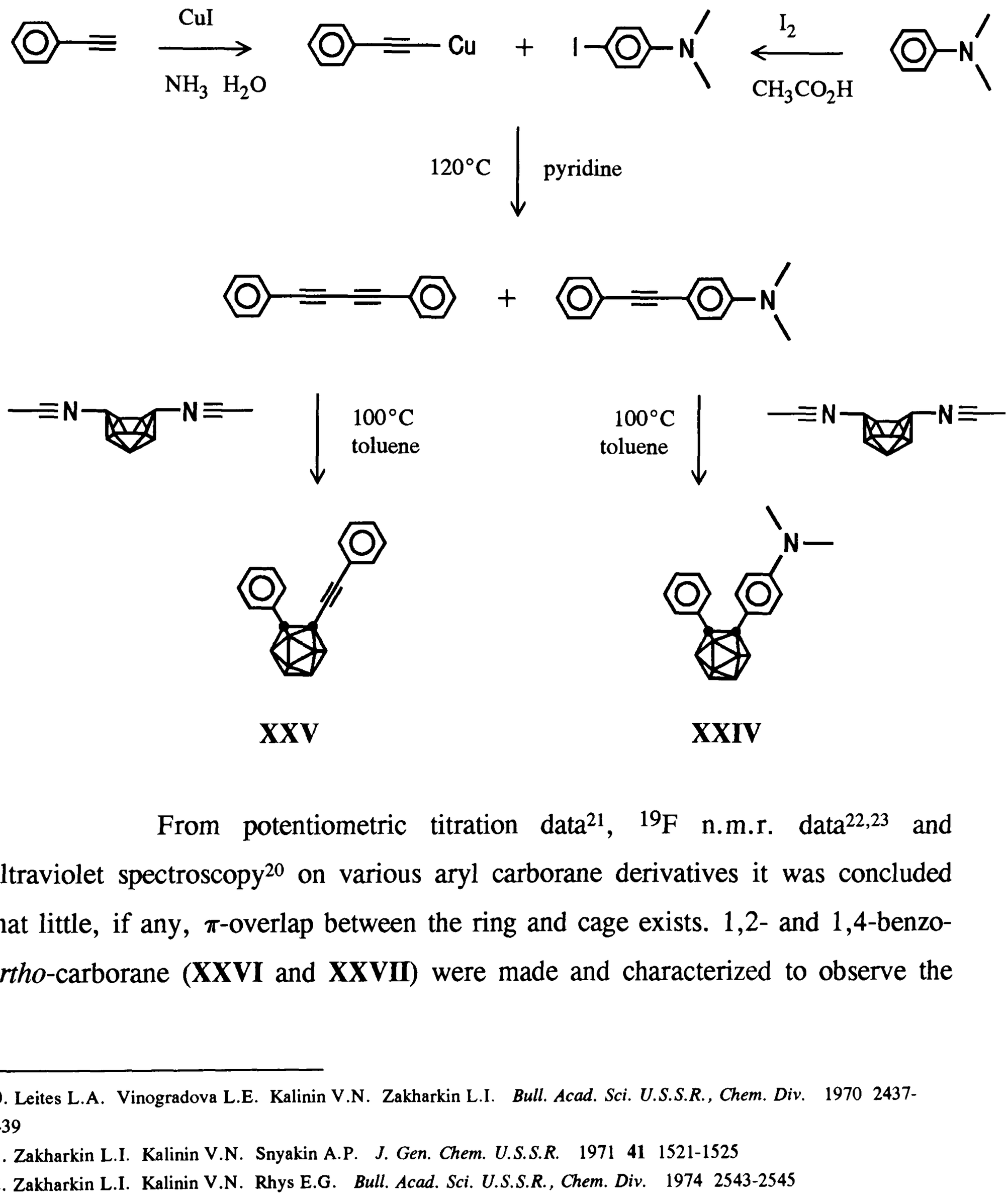


XXIV

Table of longest wavelength peaks in ultraviolet and carboranyl carbon peaks in ^{13}C n.m.r. for comparison.

compound	λ(nm)	δ(ppm)
XXII	274[20]	85.21
XXIV	310	85.85, 87.74
$PhNMe_2$	294	-

SCHEME D

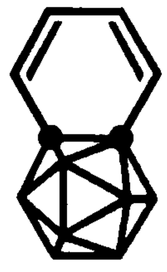


XXV **XXIV**

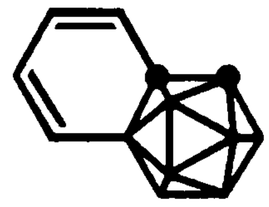
From potentiometric titration data[21], ^{19}F n.m.r. data[22,23] and ultraviolet spectroscopy[20] on various aryl carborane derivatives it was concluded that little, if any, π-overlap between the ring and cage exists. 1,2- and 1,4-benzo-*ortho*-carborane (**XXVI** and **XXVII**) were made and characterized to observe the

20. Leites L.A. Vinogradova L.E. Kalinin V.N. Zakharkin L.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1970 2437-2439
21. Zakharkin L.I. Kalinin V.N. Snyakin A.P. *J. Gen. Chem. U.S.S.R.* 1971 **41** 1521-1525
22. Zakharkin L.I. Kalinin V.N. Rhys E.G. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1974 2543-2545
23. Zakharkin L.I. Kalinin V.N. Snyakin A.P. Kvasov B.A. *J. Gen. Chem. U.S.S.R.* 1970 **40** 2406-2410

aromaticity of the rings[24,25]. It was also deduced from these studies that there was little resonance in the benzo substituent.

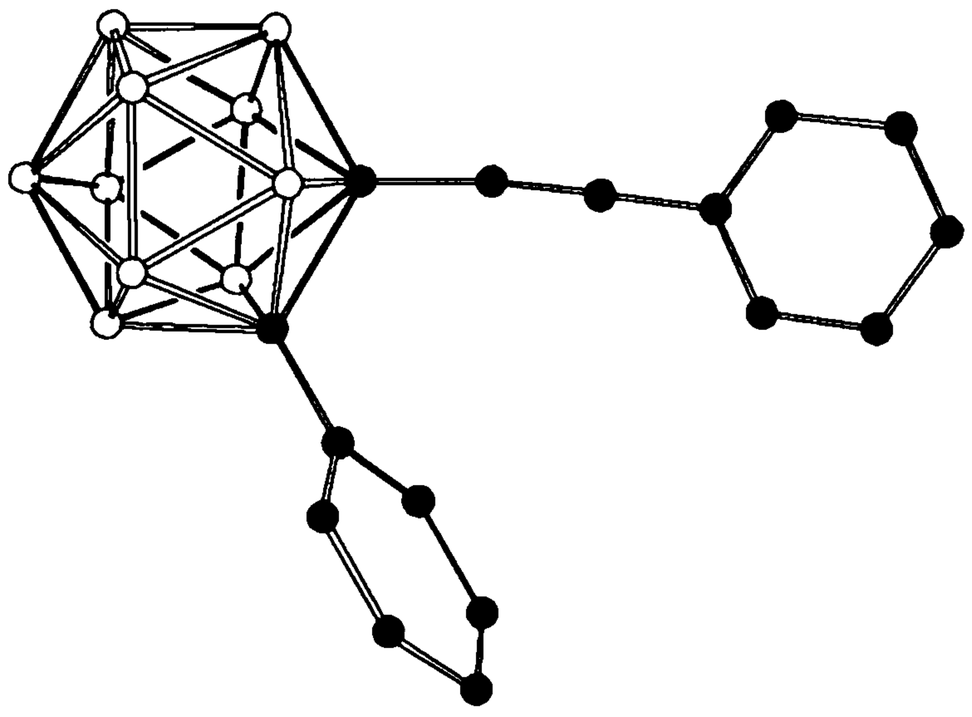


XXVI



XXVII

During the synthesis of 1-phenyl-2-(4-dimethylamino)-*ortho*-carborane a substantial amount of 1,4-diphenylbutadiyne was produced from the reaction between phenylethynyl copper and 4-(N,N-dimethylamino)-1-iodobenzene. The butadiyne was treated with bis(acetonitrile)-decaborane to produce 1-phenyl-2-phenylethynyl-*ortho*-carborane (**XXV**). X-ray studies on the latter derivative showed no unusual features; the C−C bond distances all fell within normal ranges for the coordination numbers and bond orders involved.

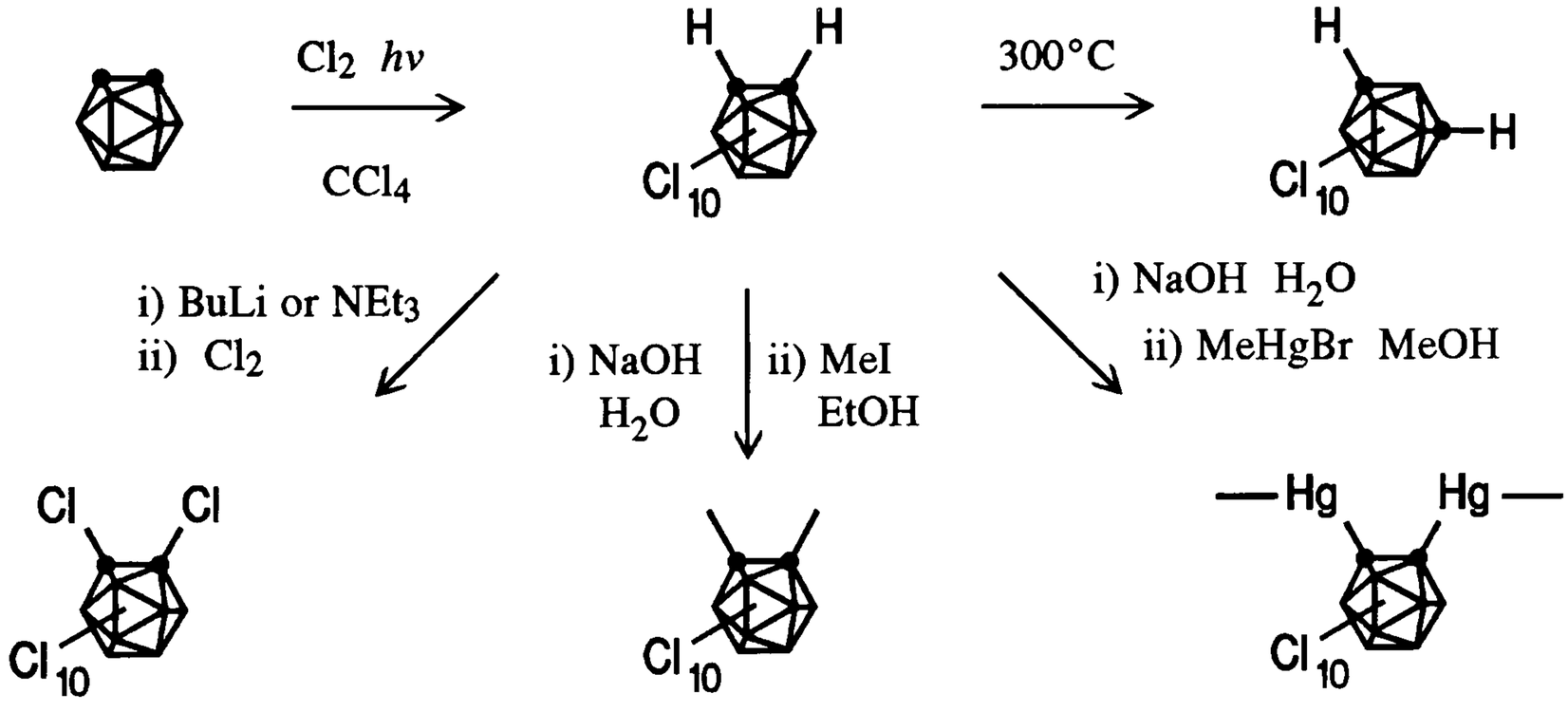


X-ray structure of **XXV**

24. Matteson D.S. Hota N.K. *J. Am. Chem. Soc.* 1971 **93** 2893-2897
25. Wu S-h Jones M.Jr. *Inorg. Chem.* 1988 **27** 2005-2008

BORON-DECACHLORO CARBORANES

Decachlorocarboranes are made from exhaustive photochemical, probably radical, chlorination[26,27,28,29,30] of carboranes or chlorine monofluoride[31] with carboranes. Replacing hydrogen atoms attached to cage borons with chlorine atoms increases the positive charge of the carboranyl carbons. The pK_a values in 50% ethanol of decachloro-*ortho*-carborane and decachloro-*meta*-carborane are 6.89 and 9.19 respectively[29]. These derivatives are soluble in weak alkali[28,30] and form adducts with Lewis bases and amines[29,32,33]. An X-ray study of the 1:1 3,4,5,6,7,8,9,10,11,12-decachloro-*ortho*-carborane : dimethyl sulphoxide adduct showed a cyclic arrangement with two dimethyl sulphoxide molecules and two carborane molecules linked by hydrogen bonds[34]. Many derivatives can be produced from decachloro-*ortho*-carborane and some examples are shown below[29,30,33,35,36].



26. Schroeder H. Heying T. Reiner J.R. *Inorg. Chem.* 1963 **2** 1092-1096
27. Zakharkin L.I. Kalinin V.N. Kvasov B.A. *J. Gen. Chem. U.S.S.R.* 1972 **42** 829-831
28. Zakharkin L.I. Stanko V.I. Klimova A.I. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1964 722
29. Zakharkin L.I. Ogorodnikova N.A. *J. Organometal. Chem.* 1968 **12** 13-22
30. Zakharkin L.I. Ogorodnikova N.A. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1966 314-316
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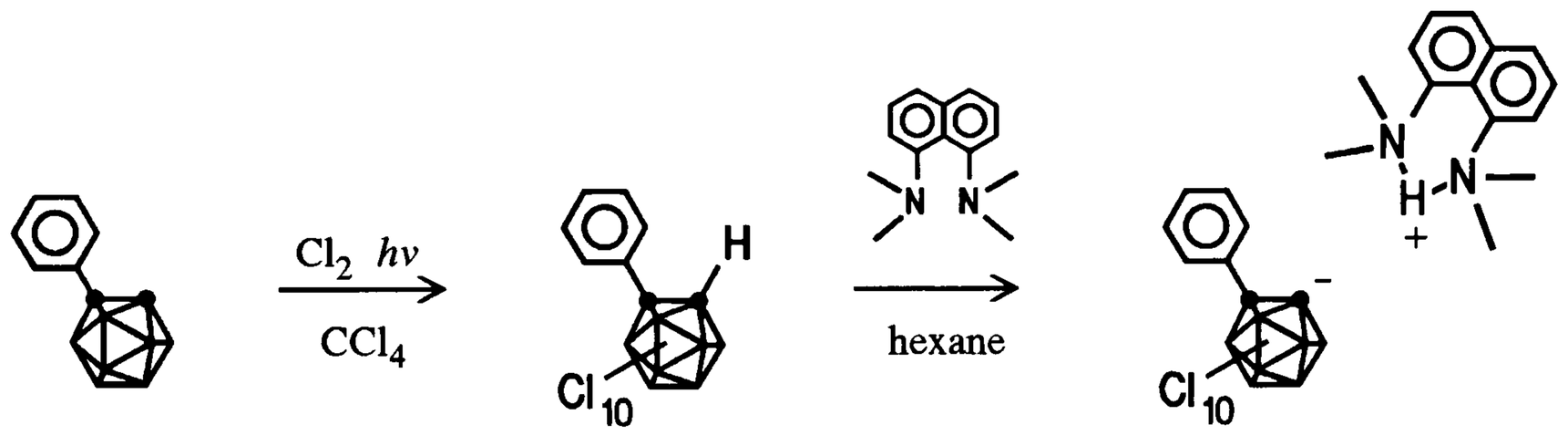
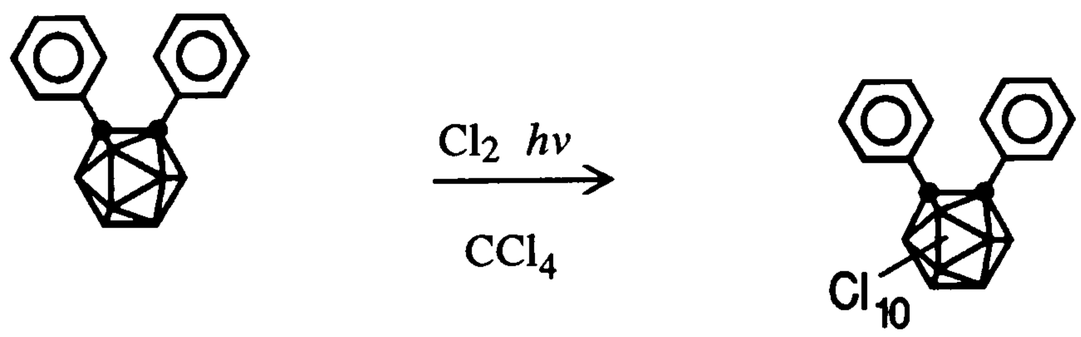
33. Schroeder H. Reiner J.R. Alexander R.P. Heying T.L. *Inorg. Chem.* 1964 **3** 1464-1465
34. Yanovskii A.I. Struchkov Yu.T. Vinogradova L.E. Leites L.A. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1982 1988-1991
35. Zakharkin L.I. Ogorodnikova N.A. *J. Gen. Chem. U.S.S.R.* 1971 **41** 568-571
36. Stanko V.I. Klimova A.I. *J. Gen. Chem. U.S.S.R.* 1966 **36** 450-453

1- phenyl- 3,4,5,6,7,8,9,10,11,12- decachloro- *ortho*- carborane (**XXVIII**), obtained by exhaustive photochemical chlorination of 1-phenyl-*ortho*-carborane, gave a 1:1 adduct with proton sponge (**XXIX**). This adduct is of great interest as if it is ionic then one carboranyl carbon would be a five coordinate carbanion. Unfortunately the powdered adduct proved to be insoluble in known solvents including water so X-ray and solution state n.m.r. studies could not be carried out to observe its ionic character. 1,2- diphenyl- 3,4,5,6,7,8,9,10,11,12- decachloro- *ortho*- carborane (**XXX**) was also successfully made by chlorination of 1,2-diphenyl-*ortho*-carborane.



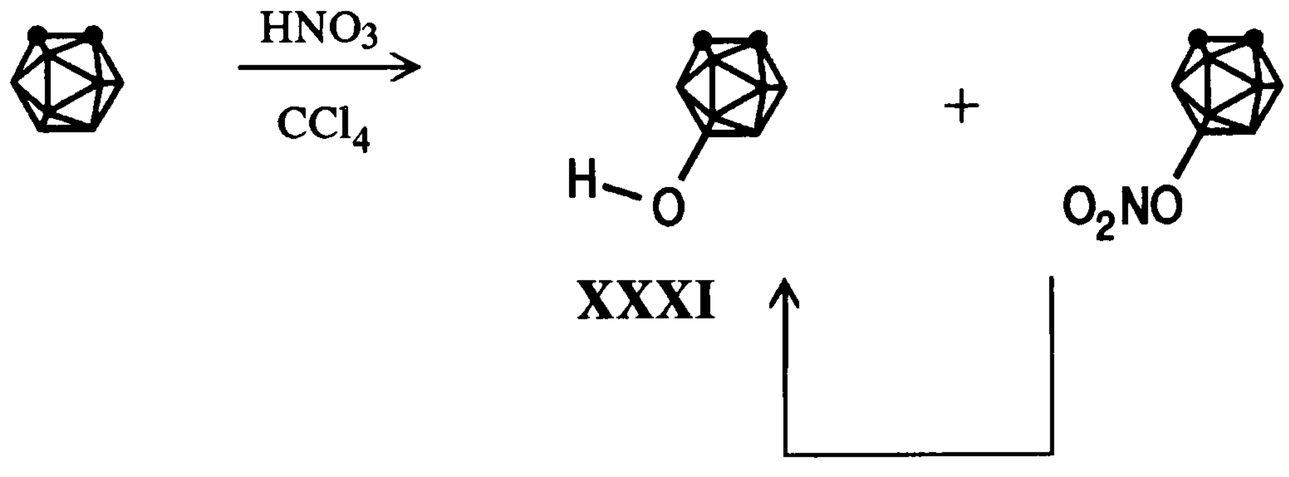
XXVIII **XXIX**

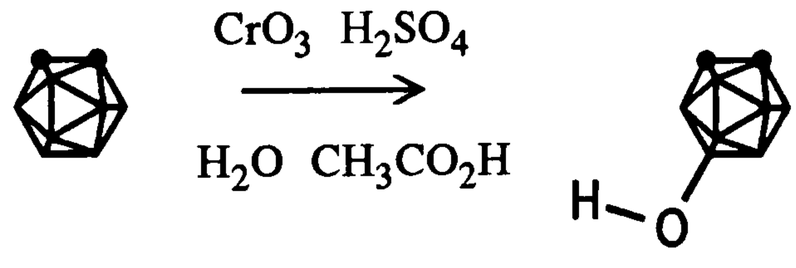


XXX

BORON-HYDROXY CARBORANES

Oxidation of carboranes by concentrated nitric acid[37,38], chromium trioxide with sulphuric acid[39] under forcing conditions, chlorosulphuric acid then lithium aluminium hydride[40] or potassium permanganate with acetic acid[41] give boron-hydroxy carboranes in low yields. 3-hydroxy-*ortho*-carborane is produced from 3-amino-*ortho*-carborane via its diazonium salt and water[42,43]. Likewise 2-hydroxy-*meta*-carborane is formed from 2-amino-*meta*-carborane[44]. Alkaline hydrolysis of phenyl(9-*meta*-carboranyl)bromonium tetrafluoroborate gives 9-hydroxy-*meta*-carborane as a minor product[45].





37. Zakharkin L.I. Kalinin V.N. Podvisotskaya L.S. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1965 1684
38. Zakharkin L.I. Kalinin V.N. Podvisotskaya L.S. *J. Gen. Chem. U.S.S.R.* 1966 **36** 1779-1781
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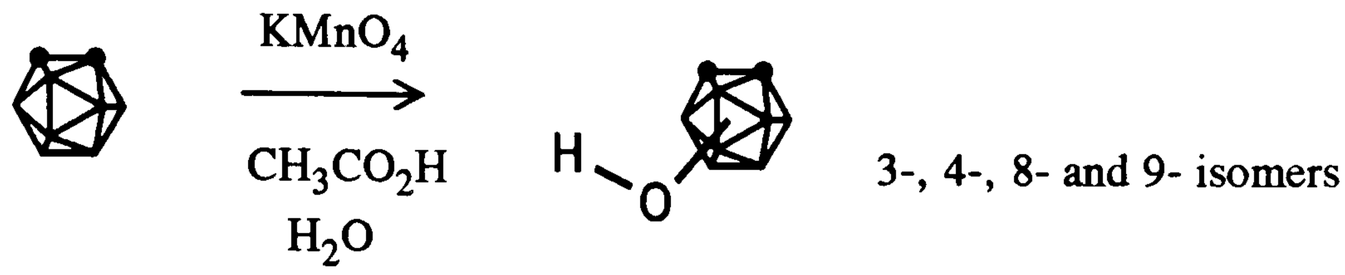
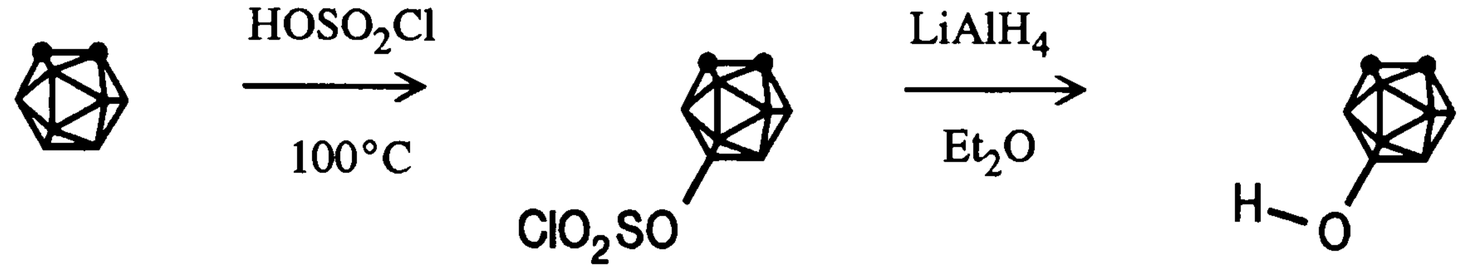
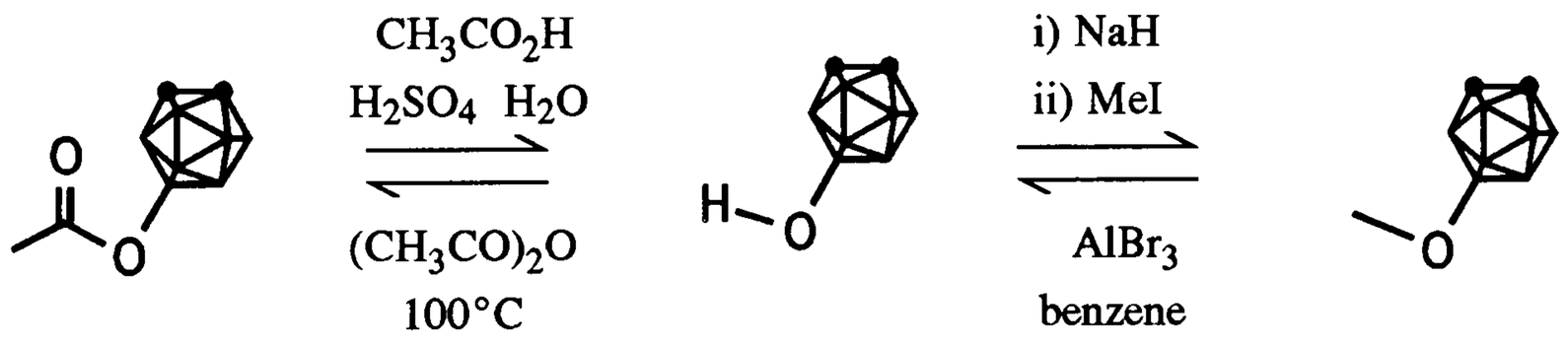


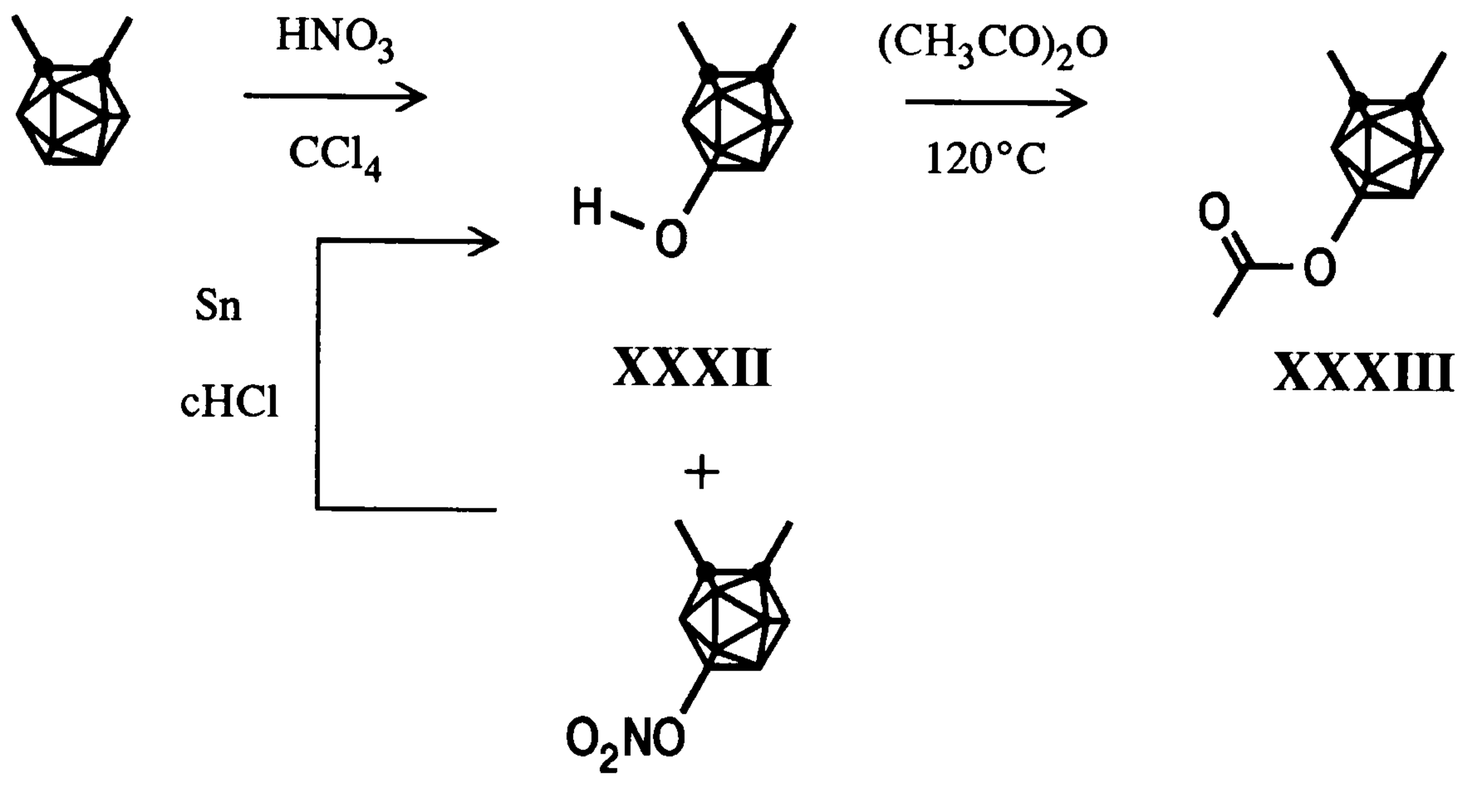


Boron-hydroxy carboranes react with acetic anhydride to form boron-acetoxy carboranes which are easily reconverted into hydroxy carboranes with acetic acid and sulphuric acid[37,39]. Boron-methoxy carboranes are produced from boron-hydroxy carboranes and diazomethane[40] or alkali metal derivatives of boron-hydroxy carboranes and methyl iodide[37,38,41]. They are converted into hydroxy carboranes with aluminium bromide in benzene[40].



A deprotonated boron-hydroxy carborane would be of interest as its molecular structure could be compared with the 1-phenyl-2-oxo-*ortho*-carborane anion structure. For X-ray studies the carboranyl carbons need to be labelled and, as phenyl groups react with nitric acid, methyl groups were used as labels. 9-hydroxy-1,2-dimethyl-*ortho*-carborane (**XXXII**) was produced from 1,2-dimethyl-*ortho*-carborane and nitric acid followed by reduction of the nitrato product with tin and hydrochloric acid. The crystals of 9-hydroxy-1,2-dimethyl-*ortho*-carborane did not

give adequate X-ray reflections for structure determination. The separation of a small amount (8%) of 8-isomer present in the product was unsuccessfully attempted by converting the hydroxy carboranes into their acetates (**XXXIII**) then using preparative gas-liquid chromatography[39]. It may be possible to separate these isomers by controlled degradation[46] or as their methyl esters by preparative gas-liquid chromatography[43].



XXXII **XXXIII**

The hydroxy compound did not produce an adduct with proton sponge which was expected as the pK_a value in 50% ethanol of a similar dervative, 9-hydroxy-*ortho*-carborane, is higher than 11.5. Attempts to form a product by deprotonation of 9-hydroxy-1,2-dimethyl-*ortho*-carborane with sodium hydride proved fruitless. The red solution formed when sodium hydride is added to the hydroxy compound is probably due to nucleophilic degradation. The anion formed then attacks the cage structure as it is a nucleophile.

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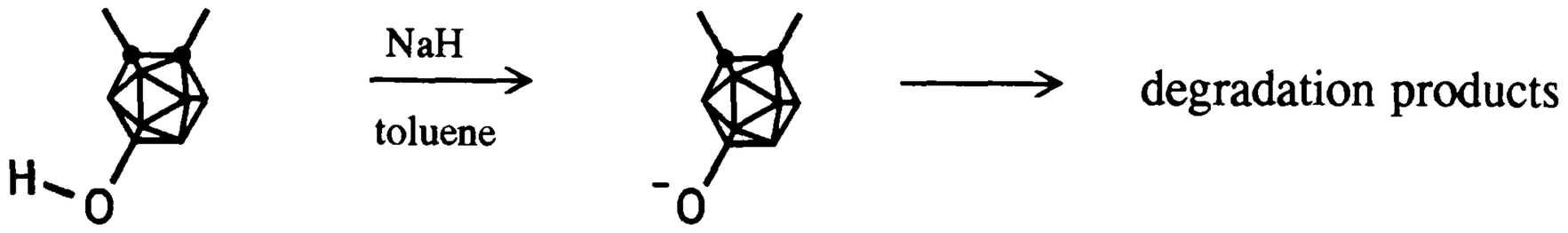
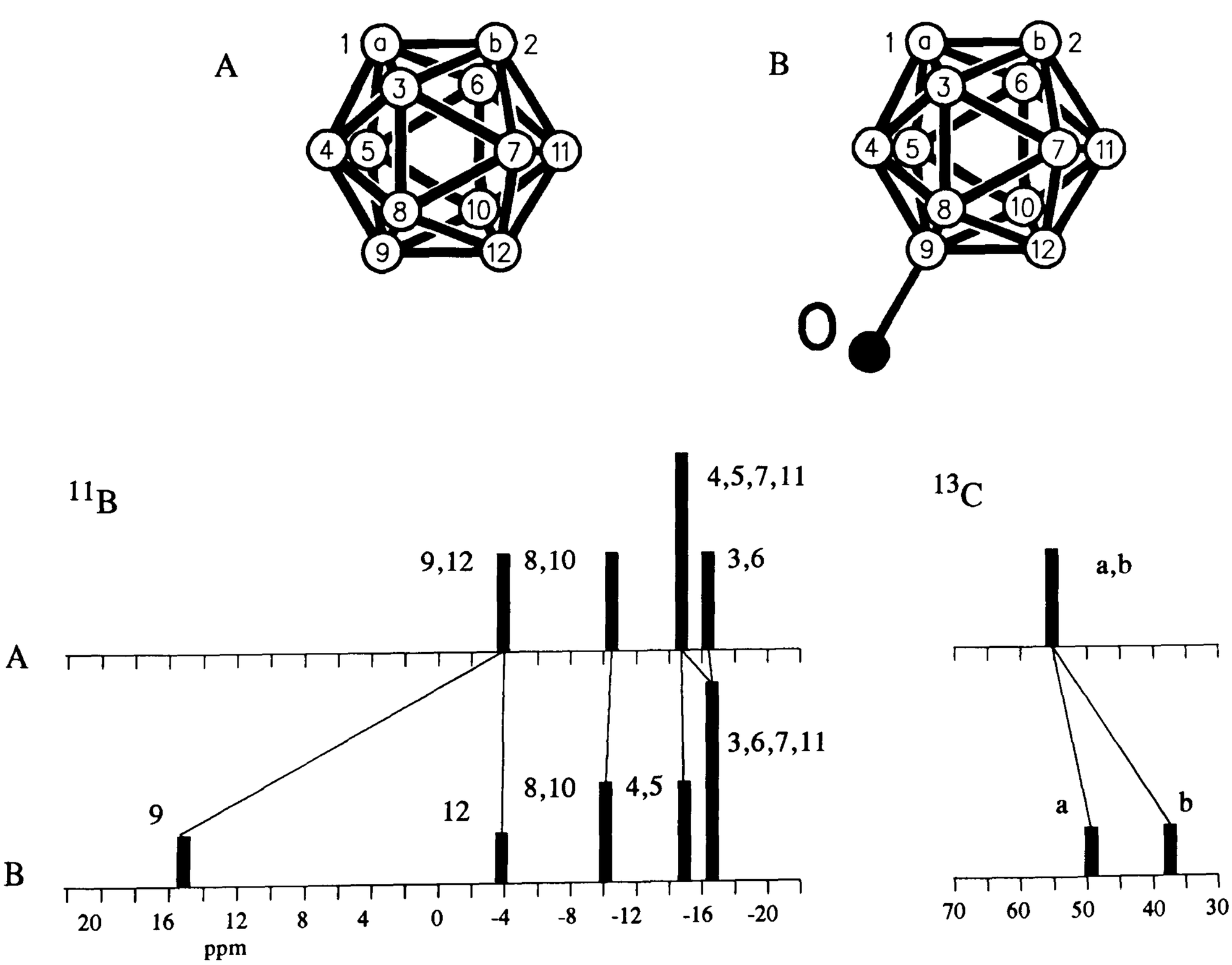
46. Stanko V.I. Babushkina T.A. Klimova T.P. Gol'tyapin Yu.V. Klimova A.I. Vasil'ev A.M. Alymov A.M. Khrapov V.V. *J. Gen. Chem. U.S.S.R.* 1976 **46** 1067-1073



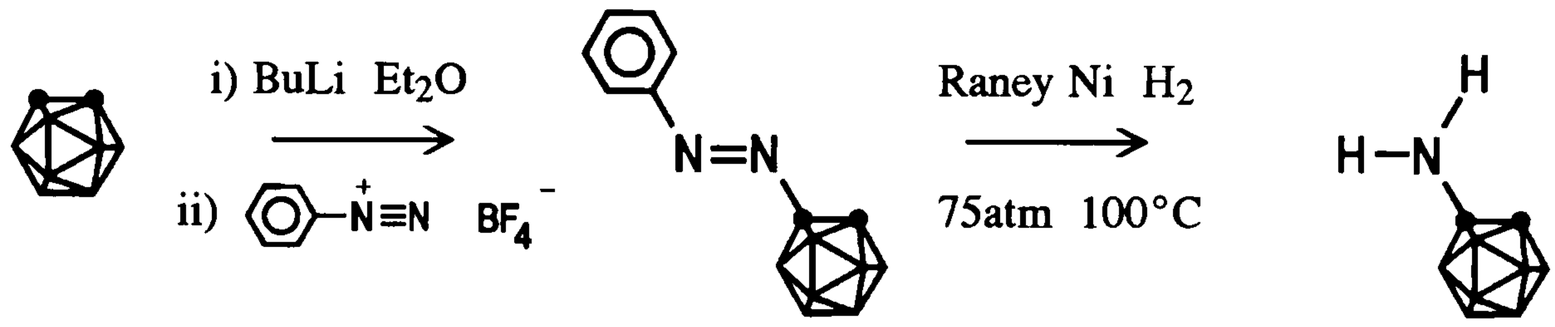
XXXII

The n.m.r. data for the hydroxy compound and 9-hydroxy-*ortho*-carborane, produced from *ortho*-carborane using the nitric acid method, showed interesting peaks. The ^{11}B n.m.r. peaks of the boron attached to oxygen is very strongly deshielded compared to other ^{11}B n.m.r. peaks found in many carborane derivatives and the ^{13}C n.m.r. peak of the carboranyl carbon opposite the boron atom attached to the hydroxy group is considerably shielded due to the antipodal effect. These results imply that the oxygen atom has a pronounced effect on the cage bonding.

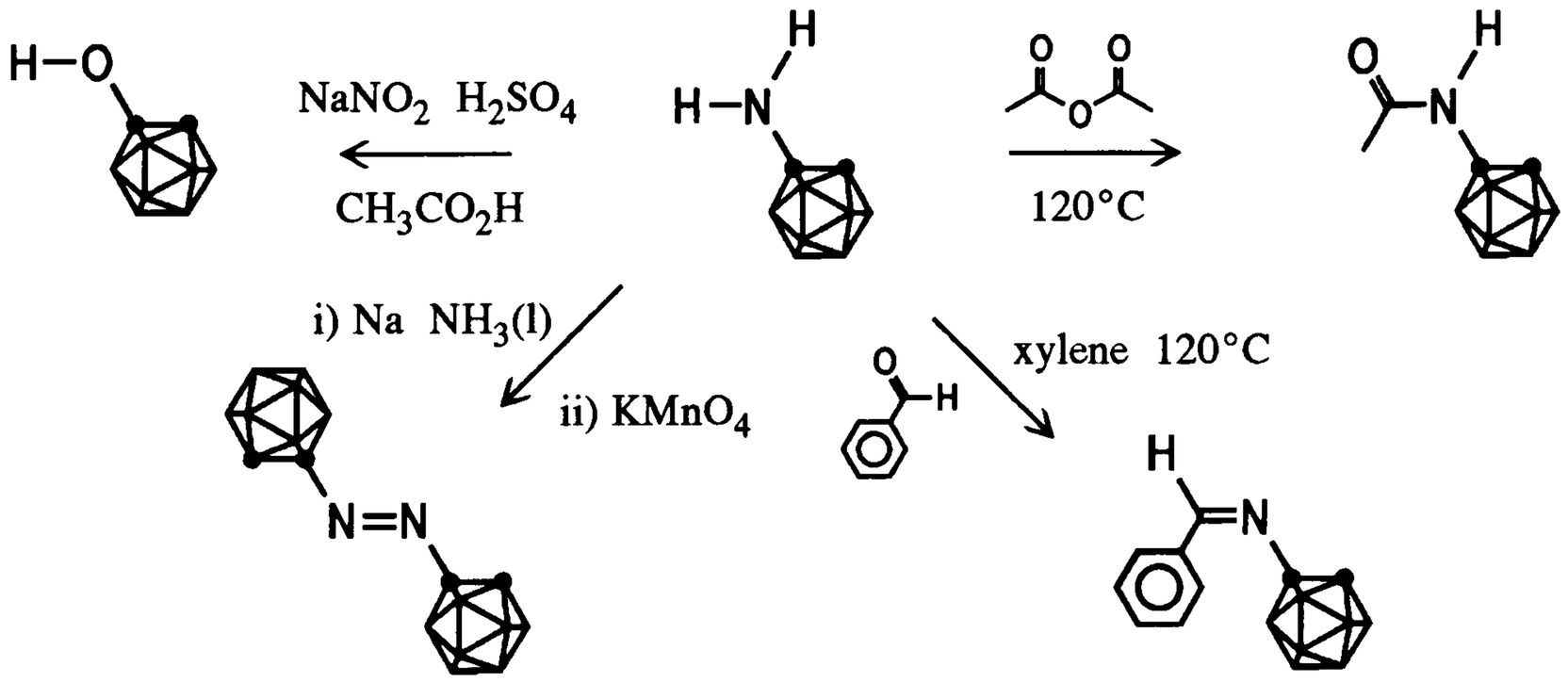


CARBON-AMINO CARBORANES

Carbon-amino carboranes were targeted as deprotonation of these derivatives may produce anions with short carbon-nitrogen bonds. 1-amino-*ortho*-carboranes are made from 1-azidocarbonyl-*ortho*-carborane[47], 1-nitroso-*ortho*-carborane[48], 1-benzeneazo-*ortho*-carborane[49] or 1-phenyl-3-(1-*ortho*-carboranyl)triazene[50]. The simplest method from *ortho*-carborane is hydrogenation of 1-benzeneazo-*ortho*-carborane made from 1-lithio-*ortho*-carborane and phenyldiazonium tetrafluoroborate.



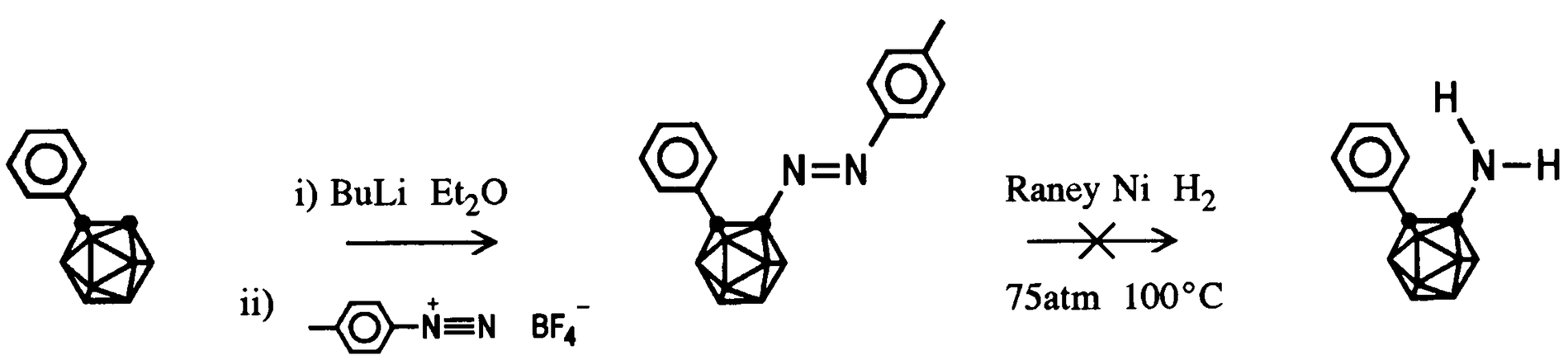
Carbon-amino carboranes are weak bases and some of their chemical properties are analogous to aliphatic amines[48]. The scheme below shows some carborane derivatives obtained from 1-amino-*ortho*-carborane[48,51].



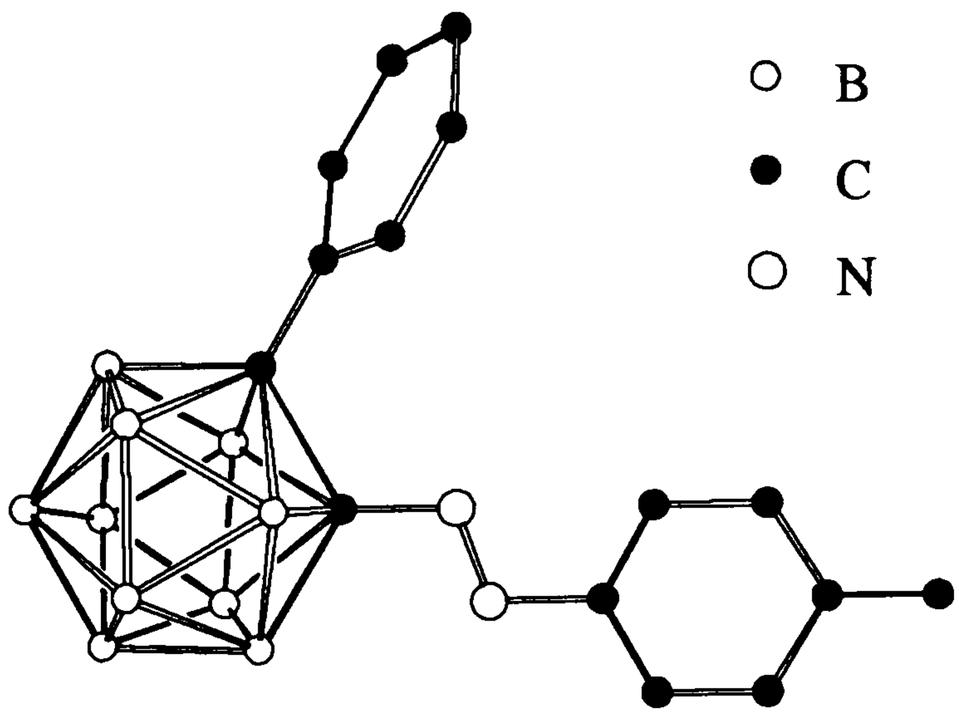
Reactions of 1-amino-*ortho*-carborane

47. Zakharkin L.I. Kalinin V.N. *J. Gen. Chem. U.S.S.R.* 1965 **35** 1878
48. Zakharkin L.I. Zhigareva G.G. *J. Gen. Chem. U.S.S.R.* 1975 **45** 1268-1275
49. Zakharkin L.I. Zhigareva G.G. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1989 179-180
50. Polyakova L.A. Bilevich K.A. Bregadze V.I. Okhlobystin O.Yu. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1972 1846

1-phenyl-2-amino-*ortho*-carborane was targeted in this study so the yellow 1-phenyl-2-(4-methylphenyl)azo-*ortho*-carborane (**XXXIV**) was readily produced from 1-phenyl-2-lithio-*ortho*-carborane and 4-methylphenyldiazonium tetrafluoroborate. The structure of the azo derivative was determined by X-ray analysis and showed a *trans* configuration with no obvious cage distortion. The compound was hydrogenated over Raney nickel in an autoclave at 100°C and 75 atmospheres of hydrogen to give a white product which did not dissolve in common solvents. A polymer is probably formed (determined by infrared spectroscopy) instead of the expected amine product perhaps due to the methyl group. Different hydrogenation conditions and reagents may give 1-phenyl-2-amino-*ortho*-carborane, which is soluble in ether and hexane[49], from the azo derivative.



XXXIV



X-ray structure of **XXXIV**

CONCLUSIONS AND FUTURE WORK

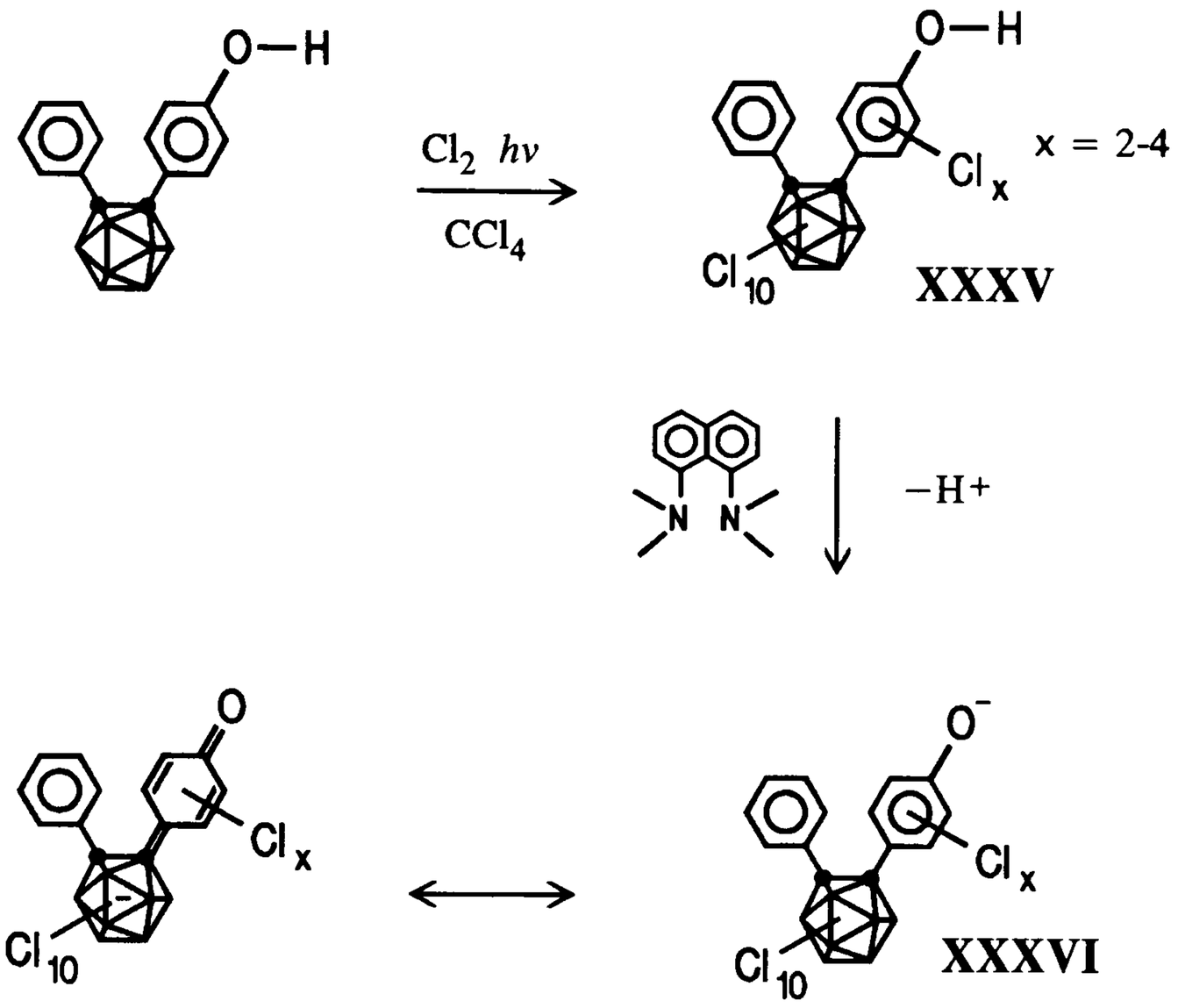
The molecular structure of a carborane anion has been successfully obtained in the case of the proton sponge salt of 1-phenyl-2-mercapto-*ortho*-carborane and found to contain similar distortions to the oxygen analogue. A proton sponge salt of 1,2-dimercapto-*ortho*-carborane was also obtained but its molecular structure remains to be determined by X-ray analysis.

Two other 1:1 carborane : proton sponge adducts were also produced from 1-phenyl-3,4,5,6,7,8,9,10,11,12-decachloro-*ortho*-carborane and 1-phenyl-7-mercapto-*meta*-carborane with proton sponge but the insolubility of the adducts in known solvents prevents use of solution state n.m.r. spectroscopy and X-ray crystallography for investigation of ionic character and molecular structure determination respectively.

An adduct of 1-phenyl-2-(4-hydroxyphenyl)-*ortho*-carborane : proton sponge could not be isolated. 1-phenyl-2-(4-dimethylaminophenyl)-*ortho*-carborane showed negligible conjugation between the ring and cage from ultraviolet and n.m.r. spectroscopy but its molecular structure, by X-ray analysis, is required before drawing conclusions.

The molecular structures of 1-phenyl-2-amino-*ortho*-carborane and its deprotonated form are worth investigating. The reduction of 1-phenyl-2-(4-methylphenyl)azo-*ortho*-carborane by other reducing agents like zinc and hydrochloric acid to form 1-phenyl-2-amino-*ortho*-carborane could probably be achieved.

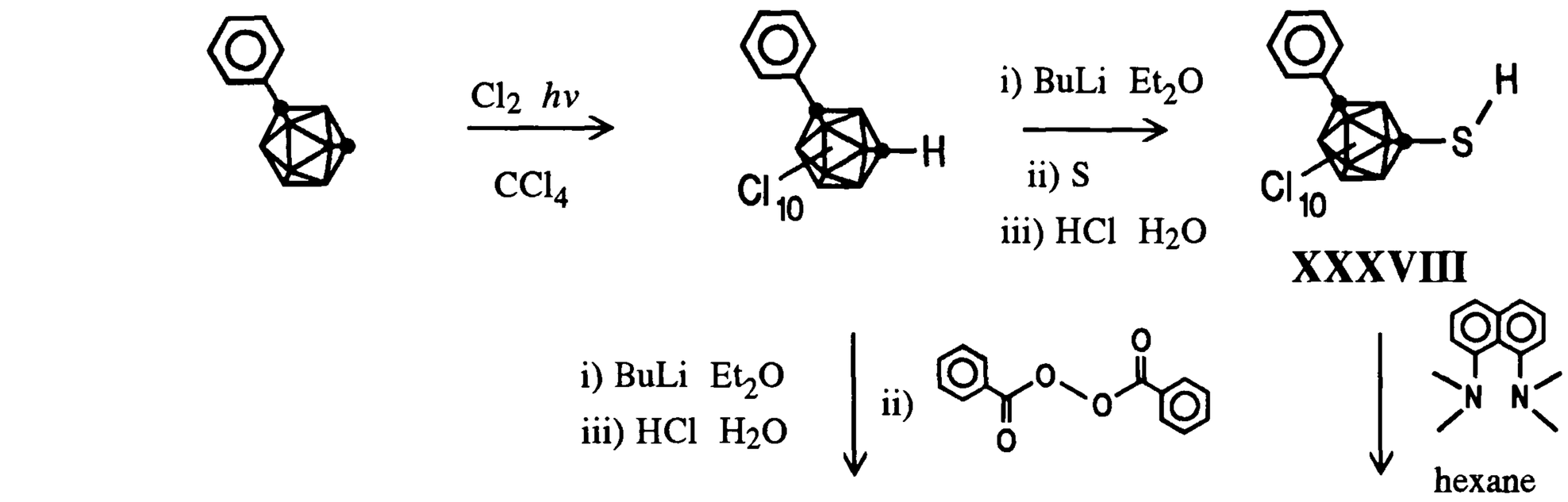
The successful formation of 1,2-diphenyl-3,4,5,6,7,8,9,10,11,12-decachloro-ortho-carborane showed that 1-phenyl-2-(4-hydroxyphenyl)-*ortho*-carborane could be chlorinated to a polychloro derivative (**XXXV**). This could then be deprotonated by proton sponge to give a salt (**XXXVI**) with π-bonding between the cage and the ring. Carbon-fluorophenyl decachlorocarboranes showed increased resonance between ring and cage compared to carbon-fluorophenyl carboranes according to calculations from ^{19}F n.m.r. data[27].

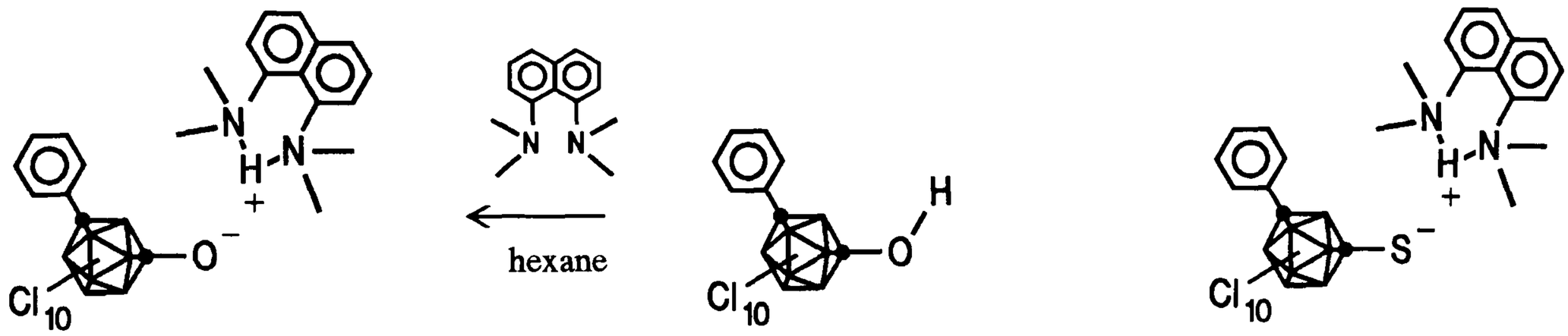


Possible formation of **XXXVI**

Other potential carborane derivatives which could form proton sponge salts with interesting molecular structures are decachlorocarboranes with hydroxy and mercapto groups present, like 1-phenyl-7-hydroxy- and 1-phenyl-7-mercapto-decachloro-*meta*-carborane (**XXXVII** and **XXXVIII**) overleaf.

9-hydroxy-*ortho*-carboranes have been made and attempts to form anions of these derivatives were unsuccessful. However their n.m.r. data showed strong antipodal effects which could give insight into the antipodal effect mechanism.



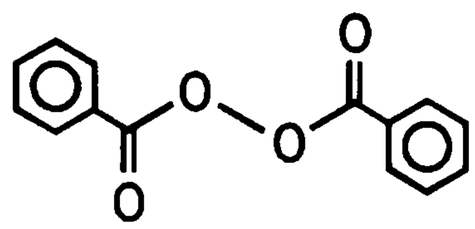


XXXVII

Possible formation of **XXXVII**, **XXXVIII** and their salts

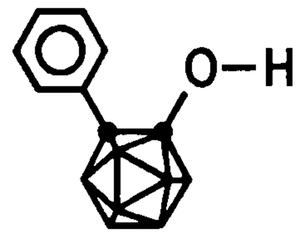
EXPERIMENTAL SECTION

Benzoyl peroxide



Anhydrous benzoyl peroxide is a very hazardous material, liable to detonate under shock, so benzoyl peroxide is commercially supplied with 25% (by weight) water for safe transit. Dry benzoyl peroxide was obtained by dissolving the required weight of peroxide (+ 25% water) in toluene, drying over anhydrous magnesium sulphate, filtering and further drying over A4 molecular sieve.

1-phenyl-2-hydroxy-1,2-dicarba-*closo*-dodecaborane



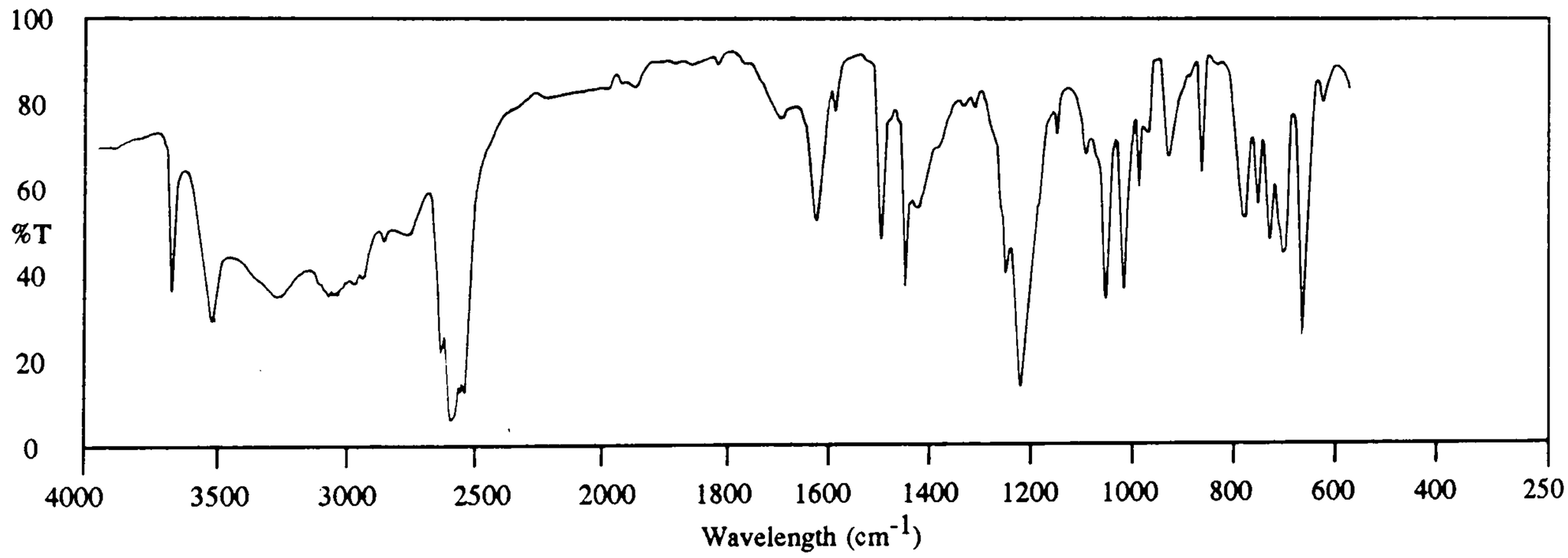
At 0°C, 7.1ml (0.01 moles) butyllithium in hexane (1.61M) was added dropwise with stirring to a solution of 2.2g (0.01 moles) of 1-phenyl-*ortho*-carborane in 20ml anhydrous diethyl ether under nitrogen. It was stirred at 20°C for one hour, cooled to 0°C and a dry solution of 2.42g (0.01 moles) benzoyl peroxide in 20ml toluene was added dropwise, turning the solution cloudy. The yellow solution was refluxed for two hours, cooled and 30ml distilled water was added dropwise. The organic layer was washed with 10% sodium hydroxide solution and the combined aqueous extracts was acidified with dilute hydrochloric acid giving a white precipitate. The aqueous suspension was extracted with diethyl ether and the combined ether extracts were washed with 5% sodium hydrogen carbonate, water, dried over anhydrous magnesium sulphate and filtered. The ether was vacuum-

removed to leave an oily residue which was vacuum distilled at 200°C and 0.01mmHg to give 0.68g (57.6%) oil. The oil became a white solid which was identified as 1-phenyl-2-hydroxy-*ortho*-carborane.

Melting point = 83-84°C (lit[12b]. = 84-86°C)

Analysis Found: C,40.6; H,7.1. $C_8H_{16}B_{10}O$ requires C,40.7; H,6.8.

Infrared (KBr disc; cm^{-1}) 3638(m), 3487(m), 3244(m), 3086(m), 3067(m), 3058(m), 3038(m), 3022(m), 2960(m), 2924(m), 2853(w), 2760(w), 2638(s), 2598(s), 2589(s), 2562(s), 2550(s), 1579(w), 1491(m), 1479(w), 1457(w), 1447(m), 1422(m), 1390(w), 1338(w), 1316(w), 1257(m), 1228(s), 1196(m), 1160(w), 1107(w), 1069(m), 1032(m), 1003(w), 988(w), 947(w), 926(w), 907(w), 883(w), 856(w), 834(w), 802(m), 777(m), 753(m), 741(m), 738(m), 691(s), 651(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 238 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 232 and 238.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

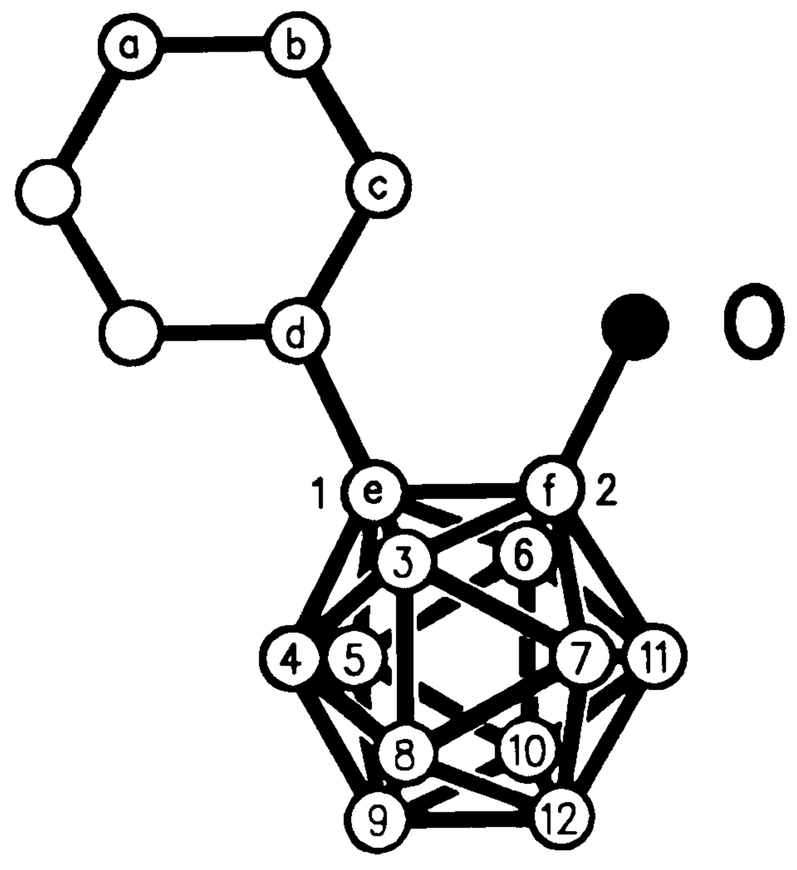
δ_{ppm}	intensity	type of peak	position of proton
7.78-7.73 7.56-7.36	5	multiplet	aromatic C-H
3.86	1	broad singlet	O-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

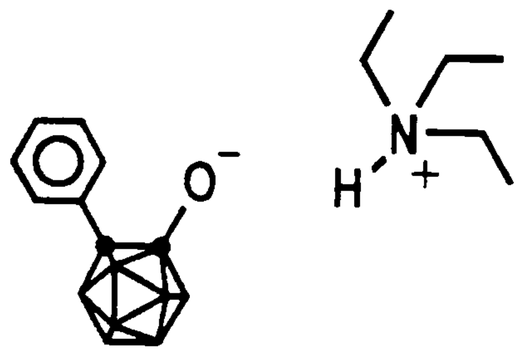
δ_{ppm}	intensity	position of boron
-4.20	1	12
-10.49	7	3,6,4,5,7,11,9
-12.88	2	8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
134.17	d
131.19	b
130.65	c
130.33	a
102.70	f
90.51	e



Triethylamine salt of 1-phenyl-2-hydroxy-1,2-dicarba-*closo*-dodecaborane

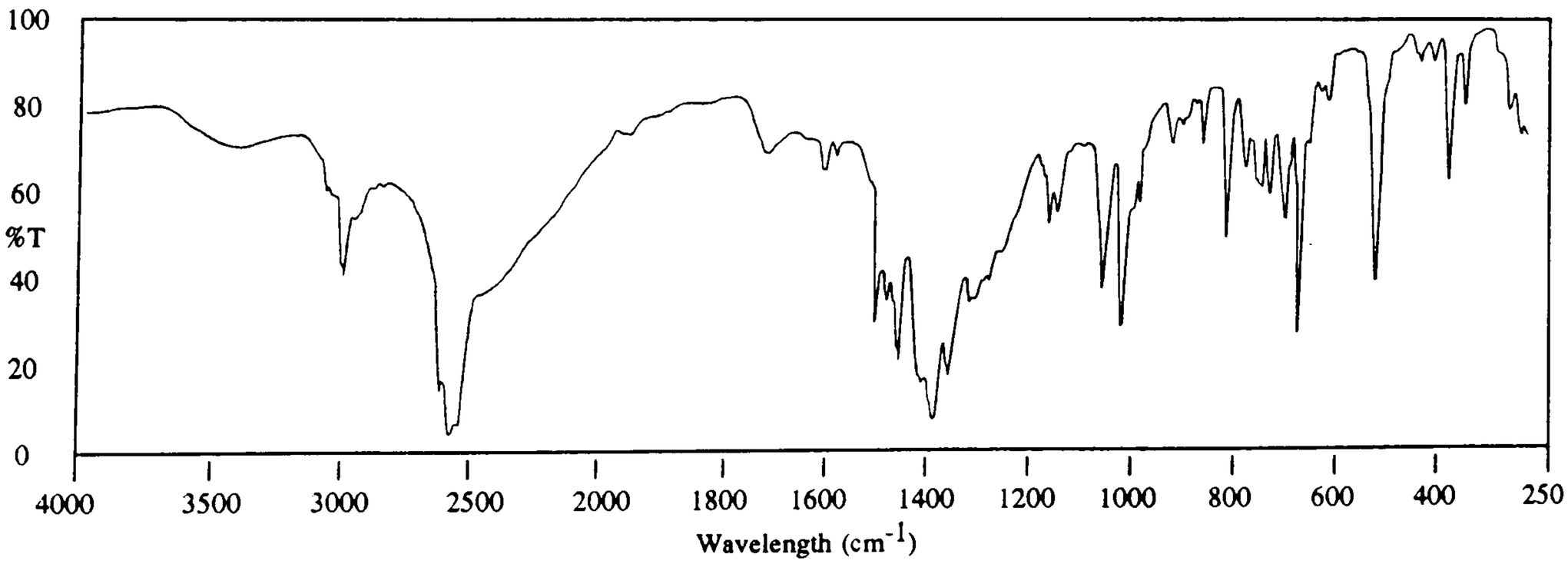


0.236g (0.001 moles) 1-phenyl-2-hydroxy-*ortho*-carborane in 5ml hexane was added dropwise with 0.3ml of triethylamine giving a gum-like precipitate. The solvents were decanted and the residue was washed with hexane and recrystallized from a toluene : hexane mixture to give 0.23g (68.2%) crystals identified as triethylamine salt of 1-phenyl-2-hydroxy-*ortho*-carborane.

Melting point = 124-126°C (lit[12c]. = 126°C)

Analysis Found: C,50.5; H,9.3; N,3.8. $C_{14}H_{31}B_{10}NO$ requires C,49.9; H,9.2; N,4.2.

Infrared (KBr disc; cm^{-1}) 3061(w), 3040(w), 3025(w), 2997(m), 2990(m), 2985(m), 2949(w), 2750-2000(m,br), 2616(s), 2574(s), 2555(s), 2547(s), 1710(w), 1603(w), 1582(w), 1498(m), 1478(m), 1462(m), 1454(m), 1451(m), 1408(m), 1392(s), 1384(s), 1358(s), 1319(m), 1316(m), 1309(m), 1295(m), 1286(m), 1264(w), 1248(w), 1193(w), 1187(w), 1177(w), 1161(w), 1113(w), 1076(m), 1047(m), 1020(w), 1007(w), 999(w), 943(w), 936(w), 928(w), 910(w), 900(w), 887(w), 838(m), 804(w), 794(w), 782(w), 776(w), 758(w), 747(w), 730(w), 726(w), 719(w), 707(w), 699(m), 682(w), 672(w), 660(w), 646(w), 552(m), 478(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 238 corresponding to the species $^{12}C_6{}^{1}H_{16}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 232 and 238. It was superimposed on a peak at m/e 101 assigned to triethylamine, $^{12}C_6{}^{1}H_{15}{}^{14}N$.

^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

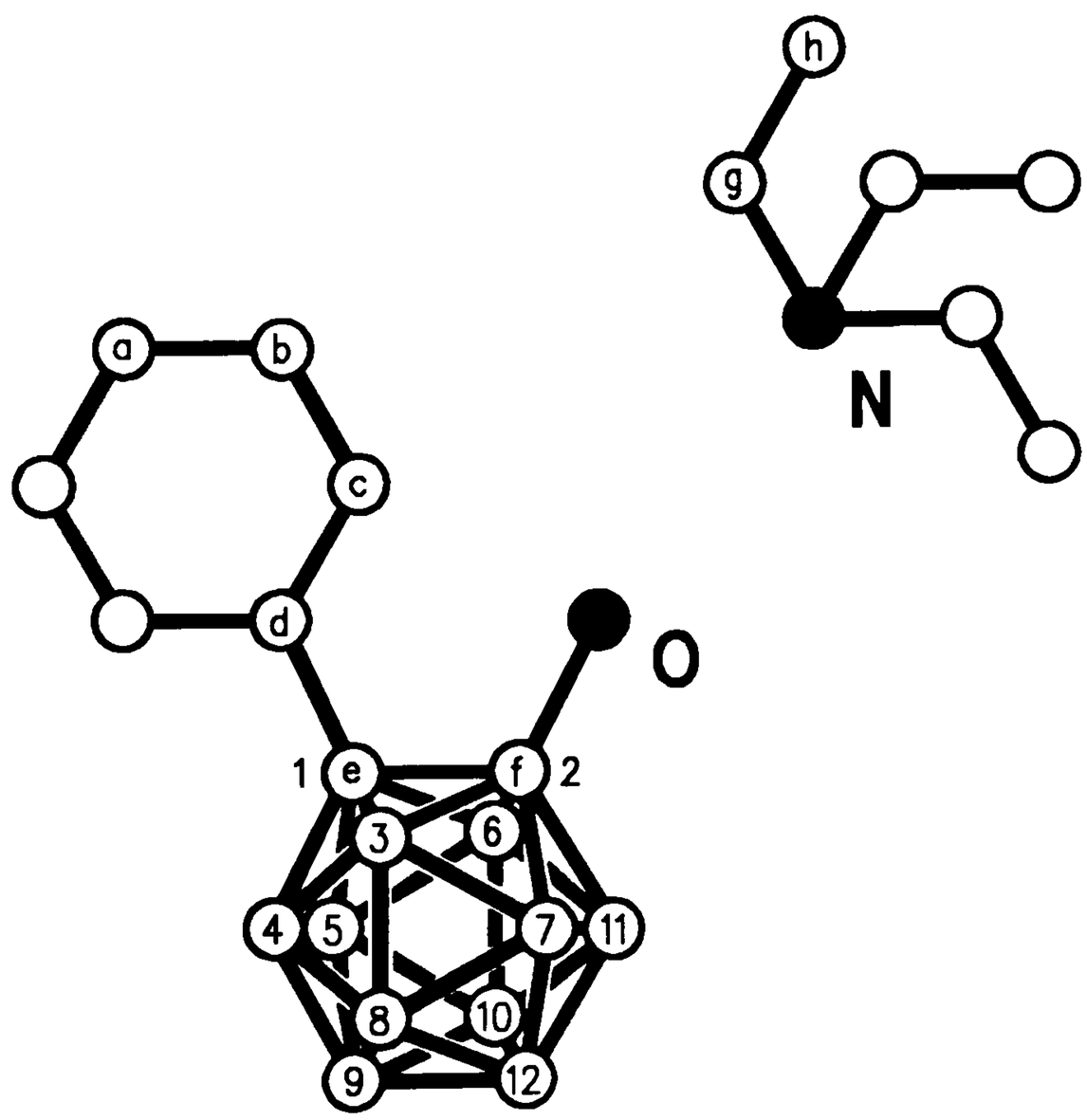
δ_{ppm}	intensity	type of peak	position of proton
7.77-7.74 7.31-7.29	5	multiplet	aromatic C(a,b,c)-H
2.77 2.74 2.71 2.68	6	doublet of doublets	ethyl C(g)-H
2.17	1	singlet	O-H
1.04 1.01 0.98	9	triplet	ethyl C(h)-H
4.0-1.1	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

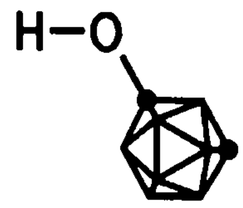
δ_{ppm}	intensity	position of boron
-8.36	1	12
-10.32	2	3,6
-13.35	4	4,5,7,11
-17.39	2	8,10
-19.31	1	9

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
135.04	d
130.80	c
129.92	f
128.56	a
127.87	b
88.52	e
45.06	g
8.03	h



1-hydroxy-1,7-dicarba-*closo*-dodecaborane

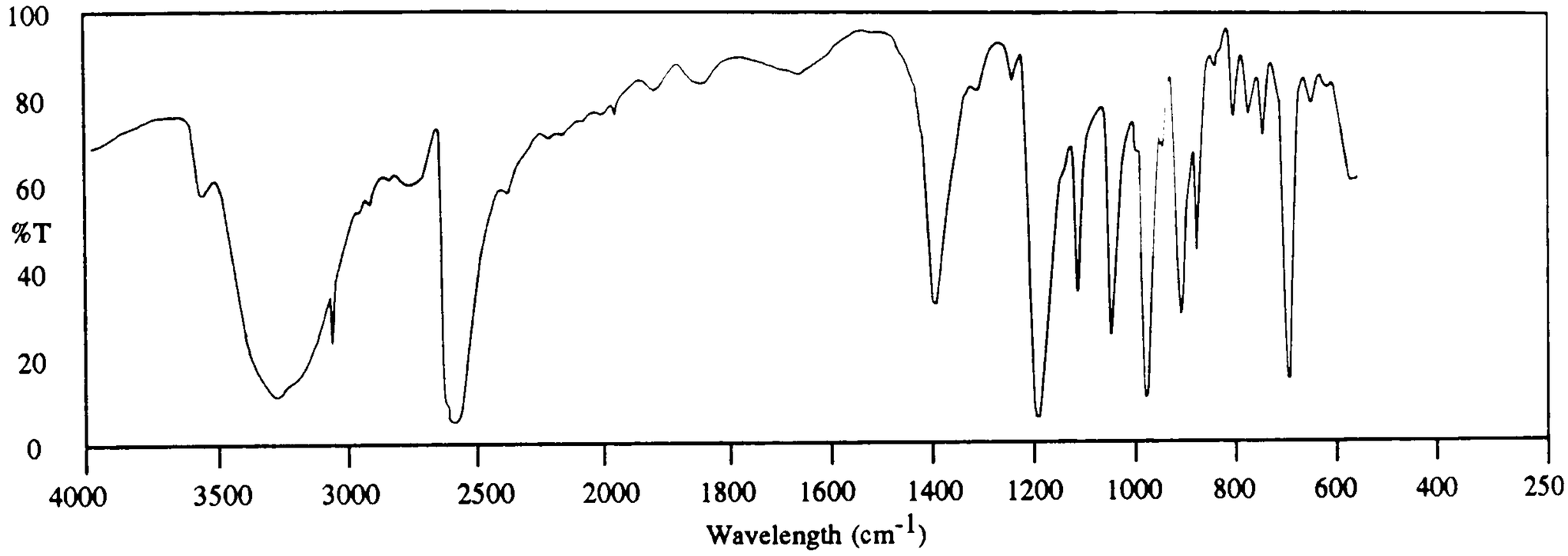


At 0°C, a solution of 1.44g (0.01 moles) sublimed *meta*-carborane in 20ml dry diethyl ether was treated dropwise with 7.1ml (0.01 moles) butyllithium in hexane (1.61M) under a dry nitrogen atmosphere. After 30 minutes stirring at 30°C, a dry solution of 2.42g (0.01 moles) benzoyl peroxide in 20ml toluene was added to the solution at 0°C. The solution was refluxed for three hours, cooled to room temperature and 30ml distilled water was added slowly. The organic layer was separated, washed with distilled water and then extracted with 20% sodium hydroxide solution. The alkali extracts were combined, acidified with dilute hydrochloric acid and the precipitate extracted with diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulphate and filtered. The ether was removed by rotary evaporator to leave a residue which was vacuum sublimed at 110°C and 0.02mmHg to give 0.57g (71.2%) of 1-hydroxy-*meta*-carborane.

Melting point = sublimes at 209-210°C (lit[8]. = 302-304°C)

Analysis Found: C,15.2; H,7.5; B,66.9. $C_2H_{12}B_{10}O$ requires C,15.0; H,7.5; B,67.5.

Infrared (KBr disc; cm^{-1}) 3540(w), 3490-2975(s), 3059(m), 2961(w), 2924(w), 2853(w), 2778(w), 2602(s), 2409(w), 2003(w), 1399(m), 1321(w), 1258(w), 1207(s), 1132(m), 1069(m), 1031(w), 1003(s), 973(w), 937(m), 908(m), 876(w), 865(w), 837(w), 808(w), 781(w), 729(s), 688(w), 661(w), 605(m).



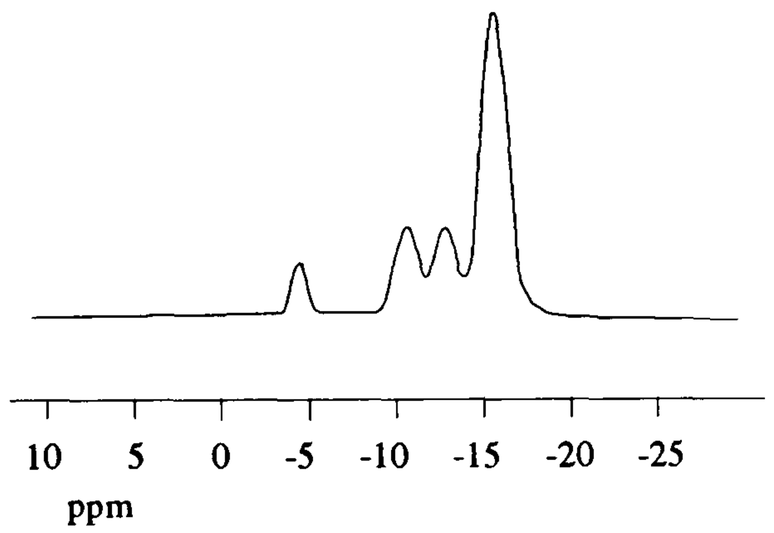
Mass spectrum (E.I.) A highest mass peak was observed at m/e 162 corresponding to the species $^{12}C_2{}^{1}H_{12}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 156 and 162.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

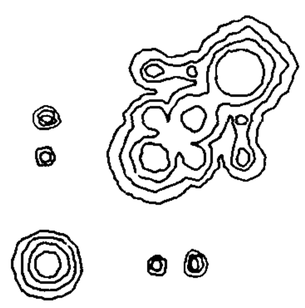
δ_{ppm}	intensity	type of peak	position of proton
3.29	1	broad singlet	O-H
2.84	1	broad singlet	carboranyl C(b)-H
4.2-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-4.30	1	5
-10.98	2	9,10
-12.79	2	8,11
-15.56	5	2,3,4,6,12

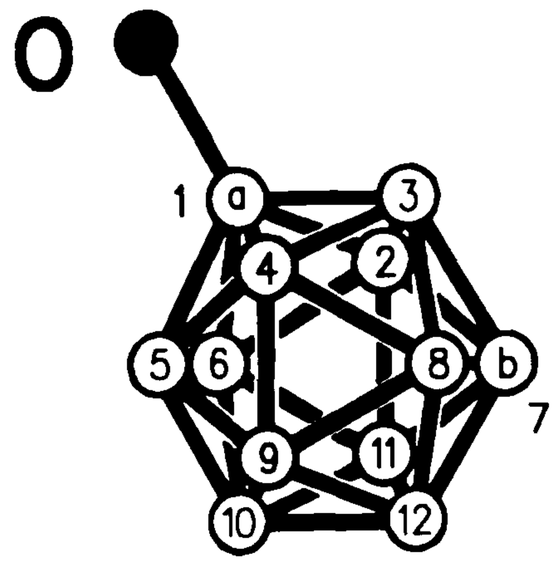


2D COSY

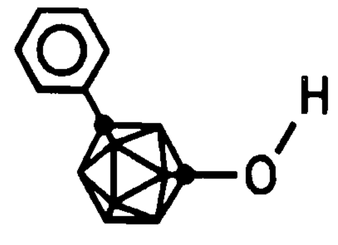


^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
101.35	a
51.59	b



1-phenyl-7-hydroxy-1,7-dicarba-*closo*-dodecaborane

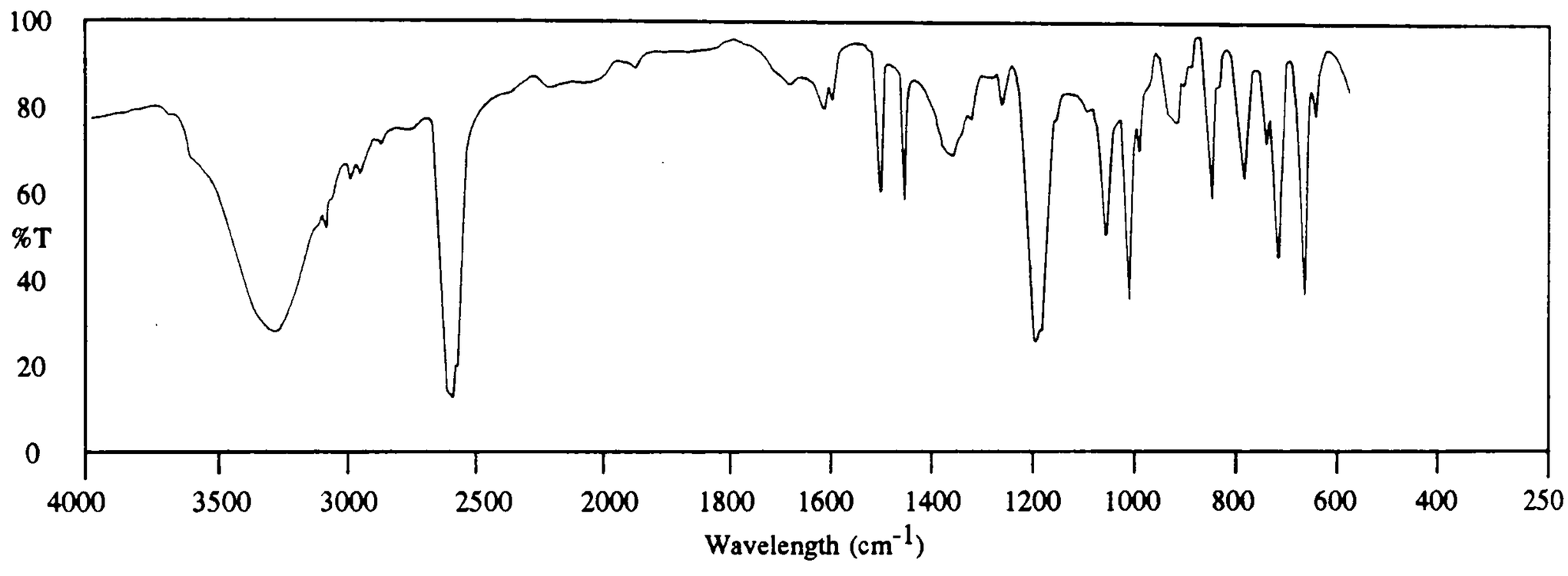


2.2g (0.01 moles) of 1-phenyl-*meta*-carborane in 20ml anhydrous diethyl ether was treated dropwise with 7.1ml (0.01 moles) butyllithium in hexane (1.61M) under a dry nitrogen atmosphere at 0°C. After 30 minutes stirring at refluxing temperature, a dry solution of 2.42g (0.01 moles) benzoyl peroxide in 20ml toluene was added to the solution at 0°C. The cloudy solution was refluxed for two hours, cooled to room temperature and 30ml distilled water was added slowly. The organic layer was separated, washed with fresh distilled water and then extracted with 20% sodium hydroxide solution. The alkali extracts were combined, acidified with dilute hydrochloric acid and the precipitate was extracted with diethyl ether. The combined ether extracts were dried over anhydrous magnesium sulphate, filtered and the ether was removed *in vacuo* to leave an oily residue. It was vacuum distilled at 155°C and 0.02mmHg to give 0.55g (46.6%) clear oil, which slowly turned solid, of 1-phenyl-7-hydroxy-*meta*-carborane.

Melting point = 71-72°C

Analysis Found: C,40.4; H,7.0; B,45.6. $C_8H_{16}B_{10}O$ requires C,40.7; H,6.8; B,45.8.

Infrared (KBr disc; cm^{-1}) 3655(w), 3570-3050(s,br), 3061(w), 3040(w), 2962(w), 2931(w), 2854(w), 2611(s), 2602(s), 2579(s), 1953(w), 1687(w), 1661(w), 1652(w), 1618(w), 1606(w), 1598(w), 1581(w), 1493(m), 1448(m), 1381(w), 1363(w), 1356(w), 1341(w), 1320(w), 1280(w), 1261(w), 1255(w), 1205(s), 1194(s), 1162(w), 1107(w), 1070(m), 1048(w), 1027(s), 1003(w), 990(w), 982(w), 943(w), 937(w), 932(w), 918(w), 904(w), 868(m), 852(w), 806(m), 762(w), 742(m), 692(s), 667(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 238 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 232 and 238.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

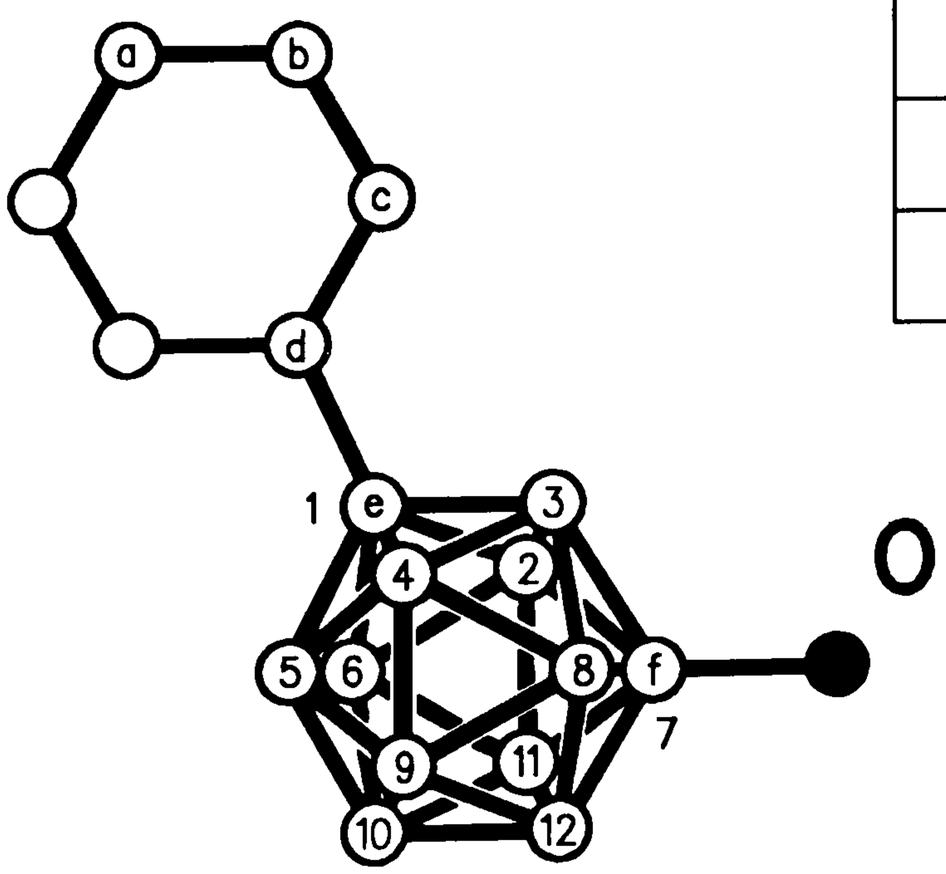
δ_{ppm}	intensity	type of peak	position of proton
7.26-7.22 6.98-6.79	5	multiplet	aromatic C(a,b,c)-H
4.1-1.0	10	broad multiplet	carboranyl B-H
0.28	1	singlet	O-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

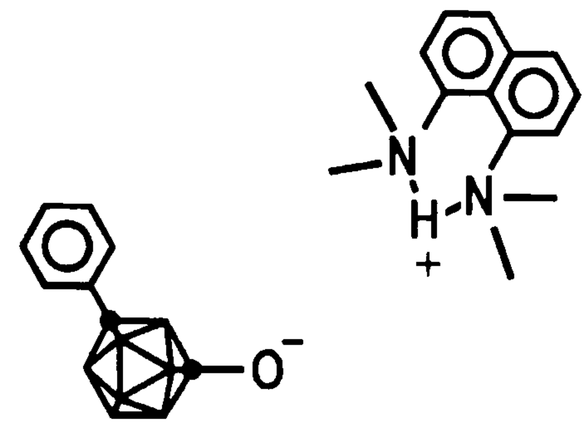
δ_{ppm}	intensity	position of boron
-6.14	1	12
-10.96	2	9,10
-12.79	7	2,3,4,6,5,8,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
134.59	d
128.76	a
128.40	c
127.82	b
101.34	f
75.00	e



Proton sponge adduct of 1-phenyl-7-hydroxy-1,7-dicarba-*closo*-dodecaborane

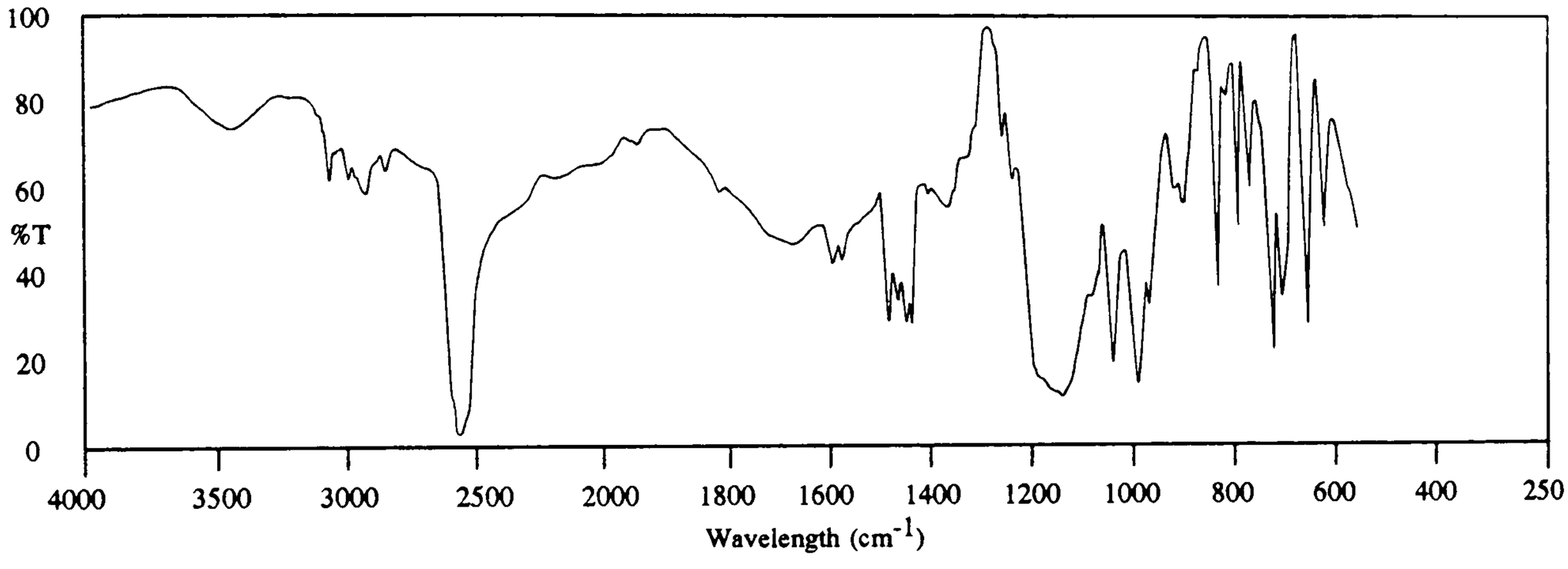


A solution of 0.236g (0.001 moles) of 1-phenyl-7-hydroxy-*meta*-carborane in 10ml hexane was mixed with 0.214g (0.001 moles) of proton sponge in 10ml hexane to yield a white precipitate which turned into a gum-like material. The solvent was decanted off and the residue washed with hexane. The residue was dissolved in a minimum amount of a 1:1 hexane : toluene mixture to give crystals identified as a 1-phenyl-7-hydroxy-*meta*-carborane : proton sponge adduct with approximately 4:1 ratio according to its elemental analysis.

Melting point = 127-128°C

Analysis Found: C,49.6; H,7.4; N,2.9. $C_{22}H_{34}B_{10}N_2O$ requires C,58.7; H,7.6; N,6.2. For 4:1 adduct, $C_{46}H_{82}B_{40}N_2O_4$ requires C,47.8; H,7.1; N,2.4.

Infrared (KBr disc; cm^{-1}) 3097(w), 3078(w), 3058(w), 3035(w), 3017(w), 2983(w), 2959(w), 2938(w), 2922(w), 2887(w), 2850(w), 2618(s), 2598(s), 2590(s), 2561(s), 1900-1400(w,br), 1592(w), 1576(w), 1491(m), 1472(m), 1448(m), 1410(w), 1379(w), 1372(w), 1340(w), 1319(w), 1269(w), 1251(w), 1218(s), 1205(s), 1185(s), 1168(s), 1159(s), 1108(m), 1072(s), 1027(s), 1002(m), 982(w), 950(w), 936(w), 902(w), 869(m), 849(w), 830(w), 808(w), 765(m), 748(m), 742(m), 697(m), 662(w), 632(w), 616(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 238 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 232 and 238. A peak of m/e 214 was also seen corresponding to proton sponge.

Attempted preparations of 1-phenyl-2-mercapto-1,2-dicarba-*closo*-dodecaborane.

METHOD A

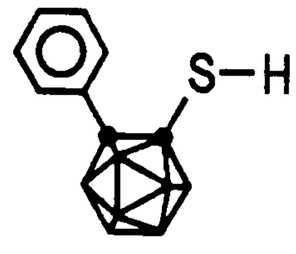
Synthesis of 2,2′-bis(1-phenyl-ortho-carboranyl) trisulphide

4.4g (0.02 moles) of 1-phenyl-*ortho*-carborane and 1.28g (0.04 moles) of powdered sulphur were added to solution of 0.96g sodium hydride (with 60% paraffin) in 40ml 1,2-dimethoxyethane under nitrogen with stirring in a fume hood. The mixture was refluxed for 10 hours, cooled and diluted with methanol. The solvents were driven off using a rotary evaporator and the residue was diluted with 20ml of distilled water and then extracted with two 10ml portions of benzene. The combined extracts were dried over anhydrous magnesium sulphate, filtered and the solvent was removed *in vacuo*. The residue was recrystallized from 40-60°C petroleum ether. 0.2g (3.7%) of crystals were formed and identified as 2,2′-bis(1-phenyl-*ortho*-carboranyl) trisulphide, $PhCB_{10}H_{10}CS_3CB_{10}H_{10}CPh$. The solvent was removed from the mother liquor by rotary evaporator to give 0.82g (16.3%) of 1-phenyl-2-mercapto-*ortho*-carborane.

METHOD B

0.1g iron (III) nitrate nonahydrate and 0.56g (0.02 moles) sodium metal were added to 50ml of liquid ammonia at -40°C with stirring using a dry ice bath for 30 minutes then a solution of 2.20g (0.01 moles) 1-phenyl-*ortho*-carborane in 20ml hexane was added. After an hour 0.32g (0.01 moles) of sulphur powder was added in small portions. The mixture was left to evaporate for 6 hours at ambient temperature. 60ml of 1:4 v/v ethanol : water mixture was added to the solid residue and the ethanol was pumped off using a rotary evaporator. The blue-black aqueous layer was filtered with charcoal, acidified with dilute hydrochloric acid and the products were extracted with hexane. The combined hexane extracts were washed with 10% potassium hydrogen carbonate solution, dried over anhydrous magnesium sulphate and filtered. The organic solvent was removed by rotary evaporator to give 2.11g (83.7%) of 1-phenyl-2-mercapto-*ortho*-carborane.

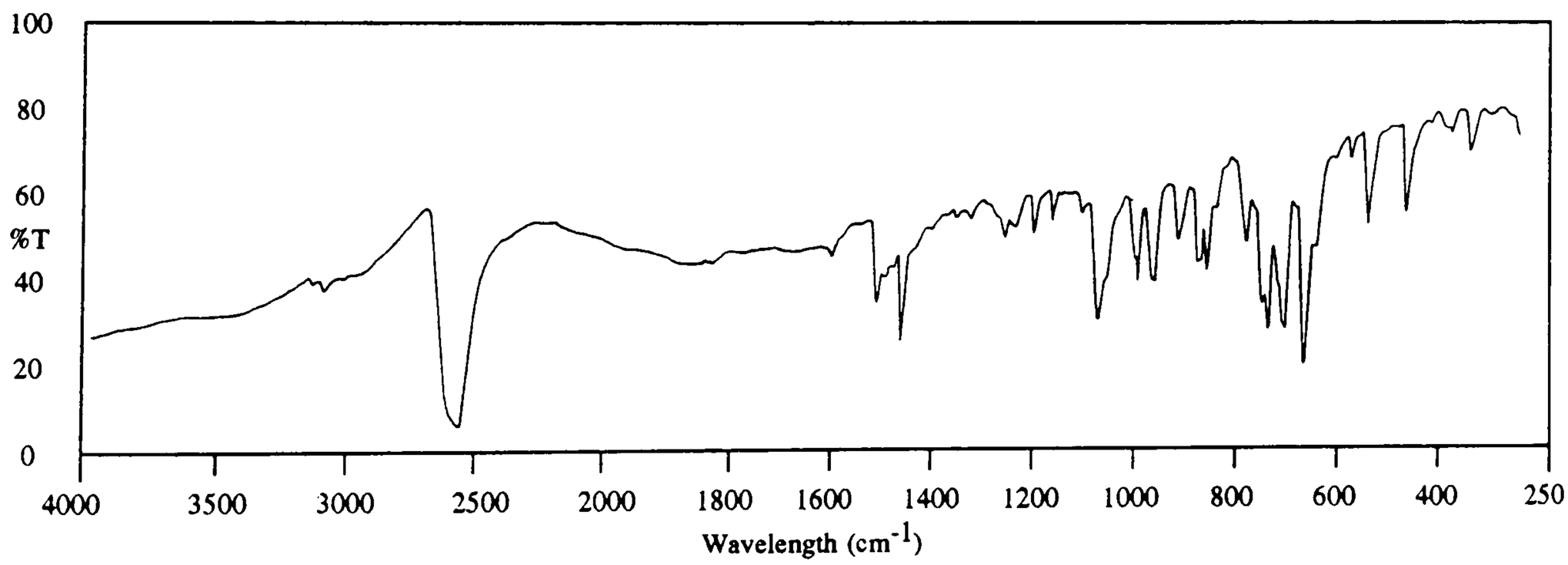
1-phenyl-2-mercapto-1,2-dicarba-*closo*-dodecaborane



Melting point = 67-68°C (lit[16]. = 67-69°C)

Analysis Found: C,38.3; H,6.7; S,12.8. $C_8H_{16}B_{10}S$ requires C,38.1; H,6.4; S,12.7.

Infrared (KBr disc; cm^{-1}) 3095(w), 3050(w), 3038(w), 2608(s), 2574(s), 2557(s), 2541(s), 1557(w), 1491(m), 1475(w), 1459(w), 1445(m), 1419(w), 1388(w), 1339(w), 1315(w), 1250(w), 1232(w), 1196(w), 1161(w), 1105(w), 1076(m), 1062(m), 1008(w), 1001(m), 972(m), 924(w), 889(w), 884(w), 871(w), 852(w), 797(w), 767(m),752(m), 734(w), 721(m), 701(w), 684(s), 665(w), 624(w), 596(w), 563(w), 490(m), 442(w), 411(w), 403(w), 368(w), 325(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 254 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{32}S$, accompanied by the usual carborane isotope distribution pattern between m/e 248 and 254.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

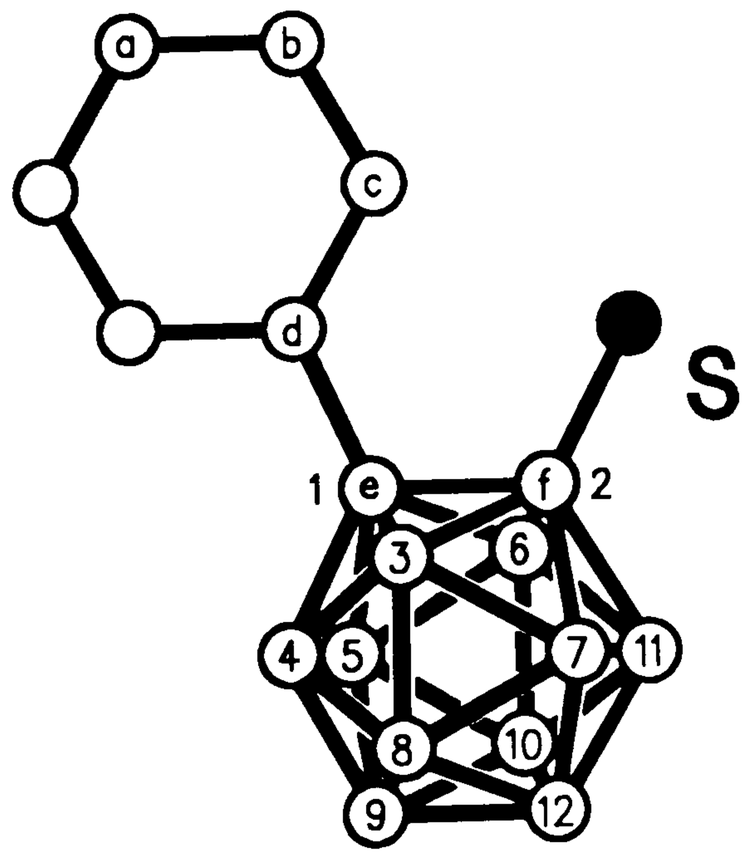
δ_{ppm}	intensity	type of peak	position of proton
7.68-7.65 7.55-7.33	5	multiplet	aromatic C-H
3.37	1	singlet	S-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent C_6D_6, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

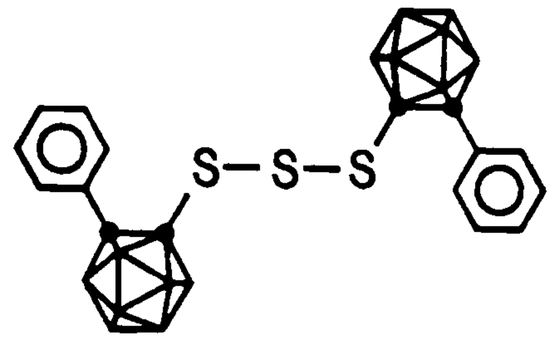
δ_{ppm}	intensity	position of boron
-1.31	1	12
-2.53	1	9
-6.85	2	8,10
-8.87	6	3,6,4,5,7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
131.59	b
131.18	d
130.87	a
128.71	c
86.63	e
84.79	f



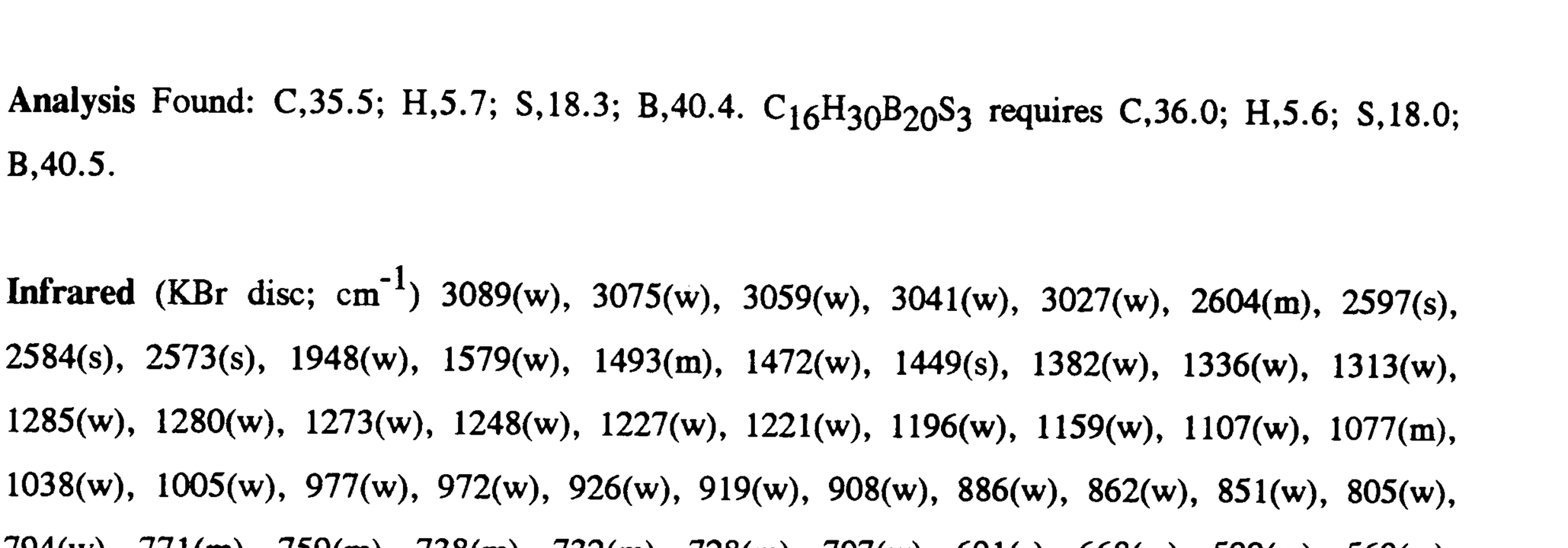
2,2′-bis(1-phenyl-1,2-dicarba-*closo*-dodecaboranyl) trisulphide



Melting point = 160-161°C

Analysis Found: C,35.5; H,5.7; S,18.3; B,40.4. $C_{16}H_{30}B_{20}S_3$ requires C,36.0; H,5.6; S,18.0; B,40.5.

Infrared (KBr disc; cm^{-1}) 3089(w), 3075(w), 3059(w), 3041(w), 3027(w), 2604(m), 2597(s), 2584(s), 2573(s), 1948(w), 1579(w), 1493(m), 1472(w), 1449(s), 1382(w), 1336(w), 1313(w), 1285(w), 1280(w), 1273(w), 1248(w), 1227(w), 1221(w), 1196(w), 1159(w), 1107(w), 1077(m), 1038(w), 1005(w), 977(w), 972(w), 926(w), 919(w), 908(w), 886(w), 862(w), 851(w), 805(w), 794(w), 771(m), 759(m), 738(m), 732(m), 728(m), 707(w), 691(s), 668(w), 599(w), 569(w), 492(m), 478(w), 410(w), 402(w), 379(w), 370(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 538 corresponding to the species $^{12}C_{16}{}^{1}H_{30}{}^{11}B_{10}{}^{32}S_3$, accompanied by the usual carborane isotope distribution pattern between m/e 524 and 538.

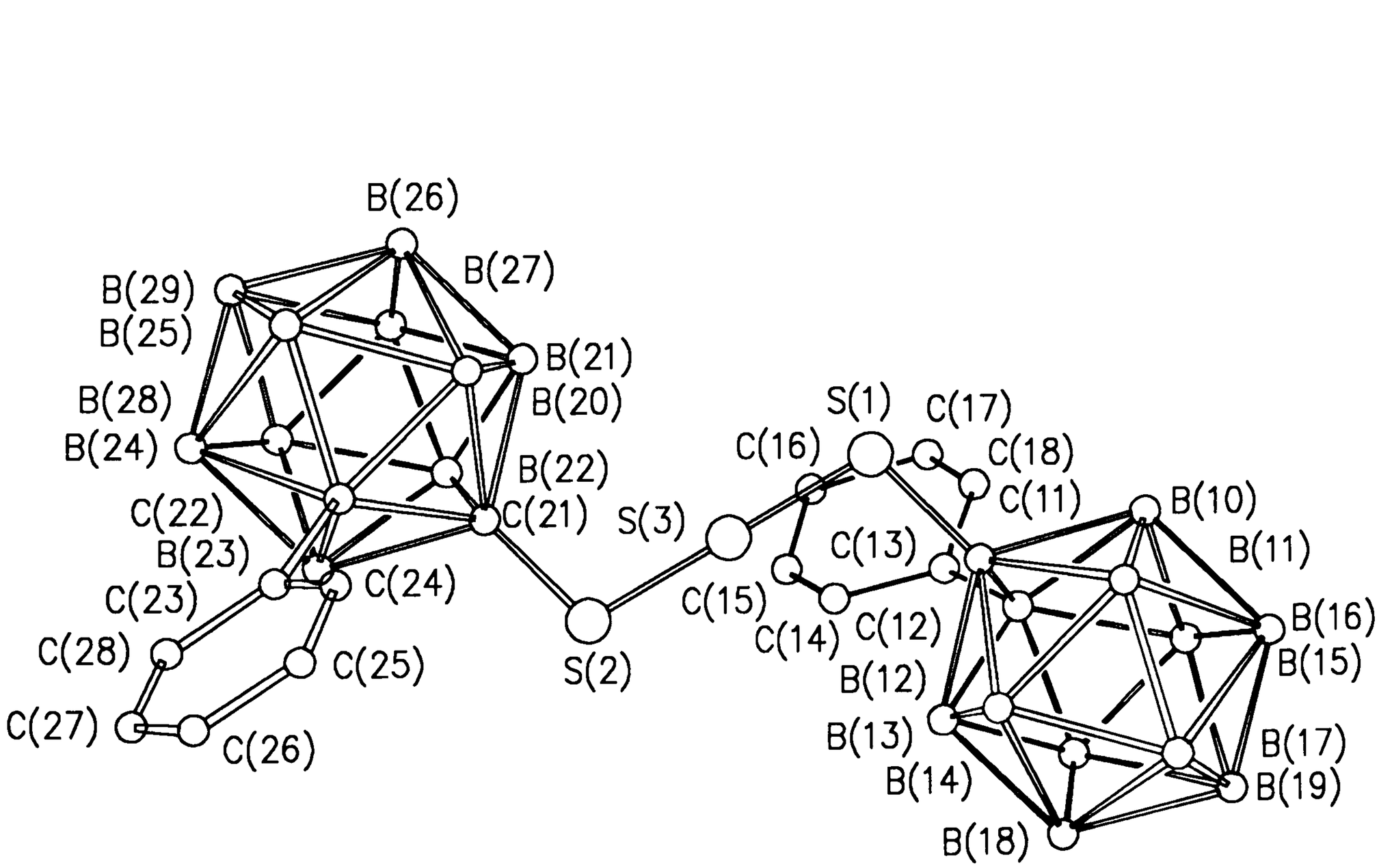
X-ray Analysis (W. Clegg, Newcastle University)

Crystallographic data, CuK_α radiation

Formula = $C_{16}H_{30}B_{20}S_3$
Formula weight, M_r = 534.8
System = orthorhombic
Space Group = $P2_12_12_1$
a = 8.0923(3)Å
b = 14.8660(7)Å
c = 24.1238(8)Å
α = 90°
β = 90°
γ = 90°
Unit cell volume, V = 2902.1Å^3
Calculated density, D_c = 1.224gcm^{-1}
Number of formulae per unit cell, Z = 4
Absorption coefficient, μ = 2.33mm^{-1}
F(000) = 1096 electrons

Number of unique reflections = 4793
Observed reflections, $F > 4\sigma_c(F)$ = 4366
$2\theta_{max}$ = 130°
Range, 2θ = 46 to 59°
Range, h = 0 to 9
Range, k = 0 to 17
Range, l = 0 to 28

Measure of overall precision of data, R_{sigma} = 0.021
Crystal size = 0.48 x 0.32 x 0.28mm
Crystal colour = colourless
Temperature, T = 295°K



Bond lengths (Å)

S(1)-C(11)	1.791(2)		S(1)-S(3)	2.036(1)
C(11)-C(12)	1.729(3)		C(11)-B(10)	1.711(3)
C(11)-B(11)	1.708(4)		C(11)-B(12)	1.695(4)
C(11)-B(13)	1.726(3)		C(12)-C(13)	1.501(3)
C(12)-B(10)	1.747(3)		C(12)-B(13)	1.733(3)
C(12)-B(14)	1.697(4)		C(12)-B(15)	1.701(3)
C(13)-C(14)	1.383(3)		C(13)-C(18)	1.391(3)
C(14)-H(14a)	0.948(29)		C(14)-C(15)	1.386(4)
C(15)-H(15a)	0.977(31)		C(15)-C(16)	1.372(4)
C(16)-H(16a)	0.816(33)		C(16)-C(17)	1.366(5)
C(17)-H(17a)	1.055(33)		C(17)-C(18)	1.377(4)
C(18)-H(18a)	0.937(27)		B(10)-H(10)	1.163(29)
B(10)-B(11)	1.786(4)		B(10)-B(15)	1.780(4)
B(10)-B(16)	1.772(5)		B(11)-H(11)	1.044(33)
B(11)-B(12)	1.775(4)		B(11)-B(16)	1.762(4)
B(11)-B(17)	1.758(5)		B(12)-H(12)	1.108(29)
B(12)-B(13)	1.788(4)		B(12)-B(17)	1.772(5)
B(12)-B(18)	1.774(4)		B(13)-H(13)	1.099(26)
B(13)-B(14)	1.787(4)		B(13)-B(18)	1.763(4)
B(14)-H(14)	1.112(28)		B(14)-B(15)	1.778(4)
B(14)-B(18)	1.783(4)		B(14)-B(19)	1.777(4)
B(15)-H(15)	1.017(28)		B(15)-B(16)	1.768(4)
B(15)-B(19)	1.764(5)		B(16)-H(16)	1.049(32)
B(16)-B(17)	1.783(5)		B(16)-B(19)	1.787(5)
B(17)-H(17)	1.058(34)		B(17)-B(18)	1.780(5)
B(17)-B(19)	1.778(4)		B(18)-H(18)	1.085(32)
B(18)-B(19)	1.784(5)		B(19)-H(19)	1.063(32)
S(2)-C(21)	1.784(2)		S(2)-S(3)	2.039(1)
C(21)-C(22)	1.741(3)		C(21)-B(20)	1.711(3)
C(21)-B(21)	1.698(3)		C(21)-B(22)	1.717(4)
C(21)-B(23)	1.719(3)		C(22)-C(23)	1.497(3)
C(22)-B(20)	1.727(3)		C(22)-B(23)	1.745(3)
C(22)-B(24)	1.710(3)		C(22)-B(25)	1.702(4)
C(23)-C(24)	1.387(3)		C(23)-C(28)	1.376(3)
C(24)-H(24a)	0.863(32)		C(24)-C(25)	1.392(5)
C(25)-H(25a)	0.962(39)		C(25)-C(26)	1.353(5)
C(26)-H(26a)	0.845(34)		C(26)-C(27)	1.361(4)
C(27)-H(27a)	1.025(32)		C(27)-C(28)	1.388(4)
C(28)-H(28a)	0.903(28)		B(20)-H(20)	1.062(27)
B(20)-B(21)	1.779(4)		B(20)-B(25)	1.786(4)
B(20)-B(26)	1.771(4)		B(21)-H(21)	1.037(27)
B(21)-B(22)	1.775(4)		B(21)-B(26)	1.774(4)
B(21)-B(27)	1.781(4)		B(22)-H(22)	0.965(29)
B(22)-B(23)	1.788(3)		B(22)-B(27)	1.760(4)
B(22)-B(28)	1.769(4)		B(23)-H(23)	1.044(27)
B(23)-B(24)	1.787(4)		B(23)-B(28)	1.763(4)
B(24)-H(24)	1.105(27)		B(24)-B(25)	1.773(4)
B(24)-B(28)	1.761(4)		B(24)-B(29)	1.765(4)
B(25)-H(25)	1.033(29)		B(25)-B(26)	1.779(4)
B(25)-B(29)	1.782(4)		B(26)-H(26)	1.128(29)
B(26)-B(27)	1.776(5)		B(26)-B(29)	1.789(4)
B(27)-H(27)	1.066(32)		B(27)-B(28)	1.787(4)
B(27)-B(29)	1.767(4)		B(28)-H(28)	1.148(28)
B(28)-B(29)	1.773(4)		B(29)-H(29)	1.061(29)

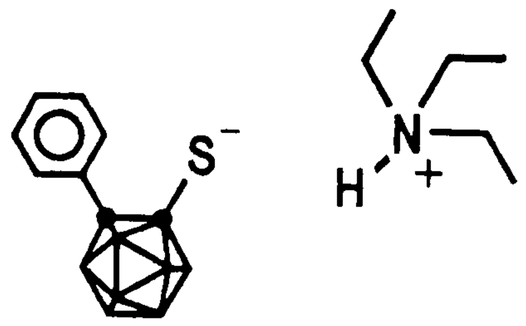
Bond angles (°)

C(11)-S(1)-S(3)	105.2(1)		S(1)-C(11)-C(12)	115.8(1)
S(1)-C(11)-B(10)	110.8(2)		C(12)-C(11)-B(10)	61.0(1)
S(1)-C(11)-B(11)	119.4(2)		C(12)-C(11)-B(11)	111.0(2)
B(10)-C(11)-B(11)	63.0(2)		S(1)-C(11)-B(12)	125.9(2)
C(12)-C(11)-B(12)	110.9(2)		B(10)-C(11)-B(12)	114.9(2)
B(11)-C(11)-B(12)	62.9(2)		S(1)-C(11)-B(13)	121.3(1)
C(12)-C(11)-B(13)	60.2(1)		B(10)-C(11)-B(13)	113.1(2)
B(11)-C(11)-B(13)	114.4(2)		B(12)-C(11)-B(13)	63.0(2)
C(11)-C(12)-C(13)	119.2(2)		C(11)-C(12)-B(10)	59.0(1)
C(13)-C(12)-B(10)	115.9(2)		C(11)-C(12)-B(13)	59.8(1)
C(13)-C(12)-B(13)	119.5(2)		B(10)-C(12)-B(13)	111.0(2)
C(11)-C(12)-B(14)	109.4(2)		C(13)-C(12)-B(14)	122.9(2)
B(10)-C(12)-B(14)	113.8(2)		B(13)-C(12)-B(14)	62.8(1)
C(11)-C(12)-B(15)	108.2(2)		C(13)-C(12)-B(15)	121.2(2)
B(10)-C(12)-B(15)	62.2(1)		B(13)-C(12)-B(15)	113.4(2)
B(14)-C(12)-B(15)	63.1(2)		C(12)-C(13)-C(14)	122.2(2)
C(12)-C(13)-C(18)	119.5(2)		C(14)-C(13)-C(18)	118.3(2)
C(13)-C(14)-H(14a)	118.2(18)		C(13)-C(14)-C(15)	120.4(2)
H(14a)-C(14)-C(15)	121.4(18)		C(14)-C(15)-H(15a)	116.8(18)
C(14)-C(15)-C(16)	120.1(3)		H(15a)-C(15)-C(16)	123.0(19)
C(15)-C(16)-H(16a)	120.1(23)		C(15)-C(16)-C(17)	120.3(3)
H(16a)-C(16)-C(17)	118.8(23)		C(16)-C(17)-H(17a)	123.5(18)
C(16)-C(17)-C(18)	119.9(3)		H(17a)-C(17)-C(18)	116.5(17)
C(13)-C(18)-C(17)	120.9(2)		C(13)-C(18)-H(18a)	118.6(18)
C(17)-C(18)-H(18a)	120.4(18)		C(11)-B(10)-C(12)	60.0(1)
C(11)-B(10)-H(10)	116.4(13)		C(12)-B(10)-H(10)	117.4(13)
C(11)-B(10)-B(11)	58.4(1)		C(12)-B(10)-B(11)	106.6(2)
H(10)-B(10)-B(11)	123.1(13)		C(11)-B(10)-B(15)	105.4(2)

C(12)-B(10)-B(15)	57.7(1)	H(10)-B(10)-B(15)	125.9(13)
B(11)-B(10)-B(15)	107.2(2)	C(11)-B(10)-B(16)	104.6(2)
C(12)-B(10)-B(16)	104.8(2)	H(10)-B(10)-B(16)	131.5(13)
B(11)-B(10)-B(16)	59.4(2)	B(15)-B(10)-B(16)	59.7(2)
C(11)-B(11)-B(10)	58.6(1)	C(11)-B(11)-H(11)	119.3(17)
B(10)-B(11)-H(11)	119.1(17)	C(11)-B(11)-B(12)	58.2(2)
B(10)-B(11)-B(12)	107.5(2)	H(11)-B(11)-B(12)	120.4(17)
C(11)-B(11)-B(16)	105.1(2)	B(10)-B(11)-B(16)	59.9(2)
H(11)-B(11)-B(16)	125.6(17)	B(12)-B(11)-B(16)	108.8(2)
C(11)-B(11)-B(17)	104.8(2)	B(10)-B(11)-B(17)	108.2(2)
H(11)-B(11)-B(17)	126.9(17)	B(12)-B(11)-B(17)	60.2(2)
B(16)-B(11)-B(17)	60.9(2)	C(11)-B(12)-B(11)	58.9(2)
C(11)-B(12)-H(12)	117.8(15)	B(11)-B(12)-H(12)	122.7(16)
C(11)-B(12)-B(13)	59.3(1)	B(11)-B(12)-B(13)	108.2(2)
H(12)-B(12)-B(13)	116.1(16)	C(11)-B(12)-B(17)	104.8(2)
B(11)-B(12)-B(17)	59.4(2)	H(12)-B(12)-B(17)	129.8(16)
B(13)-B(12)-B(17)	107.6(2)	C(11)-B(12)-B(18)	105.0(2)
B(11)-B(12)-B(18)	107.8(2)	H(12)-B(12)-B(18)	125.2(15)
B(13)-B(12)-B(18)	59.3(2)	B(17)-B(12)-B(18)	60.3(2)
C(11)-B(13)-C(12)	60.0(1)	C(11)-B(13)-B(12)	57.7(1)
C(12)-B(13)-B(12)	106.4(2)	C(11)-B(13)-H(13)	116.2(14)
C(12)-B(13)-H(13)	119.3(14)	B(12)-B(13)-H(13)	120.5(14)
C(11)-B(13)-B(14)	105.6(2)	C(12)-B(13)-B(14)	57.6(1)
B(12)-B(13)-B(14)	108.3(2)	H(13)-B(13)-B(14)	127.3(14)
C(11)-B(13)-B(18)	104.2(2)	C(12)-B(13)-B(18)	105.0(2)
B(12)-B(13)-B(18)	59.9(2)	H(13)-B(13)-B(18)	130.4(14)
B(14)-B(13)-B(18)	60.3(2)	C(12)-B(14)-B(13)	59.6(1)
C(12)-B(14)-H(14)	114.3(14)	B(13)-B(14)-H(14)	119.9(14)
C(12)-B(14)-B(15)	58.6(1)	B(13)-B(14)-B(15)	107.3(2)
H(14)-B(14)-B(15)	117.6(14)	C(12)-B(14)-B(18)	105.6(2)
B(13)-B(14)-B(18)	59.2(2)	H(14)-B(14)-B(18)	130.8(14)
B(15)-B(14)-B(18)	107.2(2)	C(12)-B(14)-B(19)	105.4(2)
B(13)-B(14)-B(19)	107.3(2)	H(14)-B(14)-B(19)	128.9(14)
B(15)-B(14)-B(19)	59.5(2)	B(18)-B(14)-B(19)	60.1(2)
C(12)-B(15)-B(10)	60.2(1)	C(12)-B(15)-B(14)	58.3(1)
B(10)-B(15)-B(14)	108.3(2)	C(12)-B(15)-H(15)	119.9(16)
B(10)-B(15)-H(15)	116.4(16)	B(14)-B(15)-H(15)	123.9(16)
C(12)-B(15)-B(16)	106.9(2)	B(10)-B(15)-B(16)	59.9(2)
B(14)-B(15)-B(16)	109.1(2)	H(15)-B(15)-B(16)	121.8(16)
C(12)-B(15)-B(19)	105.7(2)	B(10)-B(15)-B(19)	108.4(2)
B(14)-B(15)-B(19)	60.2(2)	H(15)-B(15)-B(19)	127.2(16)
B(16)-B(15)-B(19)	60.8(2)	B(10)-B(16)-B(11)	60.7(2)
B(10)-B(16)-B(15)	60.4(2)	B(11)-B(16)-B(15)	108.8(2)
B(10)-B(16)-H(16)	118.7(18)	B(11)-B(16)-H(16)	119.4(18)
B(15)-B(16)-H(16)	121.8(18)	B(10)-B(16)-B(17)	107.8(2)
B(11)-B(16)-B(17)	59.4(2)	B(15)-B(16)-B(17)	107.5(2)
H(16)-B(16)-B(17)	123.8(18)	B(10)-B(16)-B(19)	107.8(2)
B(11)-B(16)-B(19)	107.7(2)	B(15)-B(16)-B(19)	59.5(2)
H(16)-B(16)-B(19)	125.1(18)	B(17)-B(16)-B(19)	59.8(2)
B(11)-B(17)-B(12)	60.4(2)	B(11)-B(17)-B(16)	59.7(2)
B(12)-B(17)-B(16)	108.0(3)	B(11)-B(17)-H(17)	120.5(19)
B(12)-B(17)-H(17)	121.1(19)	B(16)-B(17)-H(17)	121.7(19)
B(11)-B(17)-B(18)	108.3(2)	B(12)-B(17)-B(18)	59.9(2)
B(16)-B(17)-B(18)	108.1(2)	H(17)-B(17)-B(18)	122.4(19)
B(11)-B(17)-B(19)	108.3(2)	B(12)-B(17)-B(19)	108.3(2)
B(16)-B(17)-B(19)	60.2(2)	H(17)-B(17)-B(19)	122.4(19)
B(18)-B(17)-B(19)	60.2(2)	B(12)-B(18)-B(13)	60.7(2)
B(12)-B(18)-B(14)	109.1(2)	B(13)-B(18)-B(14)	60.5(2)
B(12)-B(18)-B(17)	59.8(2)	B(13)-B(18)-B(17)	108.3(2)
B(14)-B(18)-B(17)	108.1(2)	B(12)-B(18)-H(18)	121.0(17)
B(13)-B(18)-H(18)	117.6(17)	B(14)-B(18)-H(18)	119.2(17)
B(17)-B(18)-H(18)	125.3(17)	B(12)-B(18)-B(19)	107.9(2)
B(13)-B(18)-B(19)	108.1(2)	B(14)-B(18)-B(19)	59.8(2)
B(17)-B(18)-B(19)	59.9(2)	H(18)-B(18)-B(19)	124.4(17)
B(14)-B(19)-B(15)	60.3(2)	B(14)-B(19)-B(16)	108.3(2)
B(15)-B(19)-B(16)	59.7(2)	B(14)-B(19)-B(17)	108.5(2)
B(15)-B(19)-B(17)	107.9(2)	B(16)-B(19)-B(17)	60.0(2)
B(14)-B(19)-B(18)	60.1(2)	B(15)-B(19)-B(18)	107.8(2)
B(16)-B(19)-B(18)	107.8(2)	B(17)-B(19)-B(18)	60.0(2)
B(14)-B(19)-H(19)	121.8(17)	B(15)-B(19)-H(19)	117.8(17)
B(16)-B(19)-H(19)	118.6(17)	B(17)-B(19)-H(19)	123.6(17)
B(18)-B(19)-H(19)	126.3(17)	C(21)-S(2)-S(3)	105.4(1)
S(2)-C(21)-C(22)	117.7(1)	S(2)-C(21)-B(20)	122.7(1)
C(22)-C(21)-B(20)	60.0(1)	S(2)-C(21)-B(21)	124.9(1)
C(22)-C(21)-B(21)	110.6(2)	B(20)-C(21)-B(21)	62.9(2)
S(2)-C(21)-B(22)	118.2(2)	C(22)-C(21)-B(22)	110.4(2)
B(20)-C(21)-B(22)	113.7(2)	B(21)-C(21)-B(22)	62.6(2)
S(2)-C(21)-B(23)	111.6(1)	C(22)-C(21)-B(23)	60.6(1)
B(20)-C(21)-B(23)	112.3(2)	B(21)-C(21)-B(23)	114.2(2)
B(22)-C(21)-B(23)	62.7(1)	C(21)-C(22)-C(23)	118.8(2)
C(21)-C(22)-B(20)	59.1(1)	C(23)-C(22)-B(20)	119.5(2)
C(21)-C(22)-B(23)	59.1(1)	C(23)-C(22)-B(23)	116.4(2)
B(20)-C(22)-B(23)	110.2(2)	C(21)-C(22)-B(24)	108.4(2)
C(23)-C(22)-B(24)	121.8(2)	B(20)-C(22)-B(24)	113.0(2)
B(23)-C(22)-B(24)	62.3(1)	C(21)-C(22)-B(25)	108.9(2)
C(23)-C(22)-B(25)	123.5(2)	B(20)-C(22)-B(25)	62.8(1)
B(23)-C(22)-B(25)	113.0(2)	B(24)-C(22)-B(25)	62.6(1)
C(22)-C(23)-C(24)	122.3(2)	C(22)-C(23)-C(28)	119.7(2)
C(24)-C(23)-C(28)	118.0(2)	C(23)-C(24)-H(24a)	116.3(22)

C(23)-C(24)-C(25)	120.3(3)	H(24a)-C(24)-C(25)	123.3(22)
C(24)-C(25)-H(25a)	119.	C(24)-C(25)-H(25a)	119.2
H(25a)-C(25)-C(26)	120.1(23)	C(25)-C(26)-H(26a)	121.3(23)
C(25)-C(26)-C(27)	119.7(3)	H(26a)-C(26)-C(27)	118.9(23)
C(26)-C(27)-H(27a)	121.8(18)	C(26)-C(27)-C(28)	120.5(2)
H(27a)-C(27)-C(28)	117.7(18)	C(23)-C(28)-C(27)	120.8(2)
C(23)-C(28)-H(28a)	121.4(18)	C(27)-C(28)-H(28a)	117.6(18)
C(21)-B(20)-C(22)	60.8(1)	C(21)-B(20)-H(20)	115.8(15)
C(22)-B(20)-H(20)	119.5(15)	C(21)-B(20)-B(21)	58.2(1)
C(22)-B(20)-B(21)	107.5(2)	H(20)-B(20)-B(21)	119.8(15)
C(21)-B(20)-B(25)	106.5(2)	C(22)-B(20)-B(25)	57.9(1)
H(20)-B(20)-B(25)	127.4(15)	B(21)-B(20)-B(25)	108.4(2)
C(21)-B(20)-B(26)	105.0(2)	C(22)-B(20)-B(26)	105.4(2)
H(20)-B(20)-B(26)	129.6(15)	B(21)-B(20)-B(26)	59.9(2)
B(25)-B(20)-B(26)	60.0(2)	C(21)-B(21)-B(20)	58.9(1)
C(21)-B(21)-H(21)	116.4(14)	B(20)-B(21)-H(21)	118.2(15)
C(21)-B(21)-B(22)	59.2(1)	B(20)-B(21)-B(22)	107.7(2)
H(21)-B(21)-B(22)	120.1(15)	C(21)-B(21)-B(26)	105.4(2)
B(20)-B(21)-B(26)	59.8(2)	H(21)-B(21)-B(26)	127.6(15)
B(22)-B(21)-B(26)	107.6(2)	C(21)-B(21)-B(27)	105.1(2)
B(20)-B(21)-B(27)	107.4(2)	H(21)-B(21)-B(27)	129.3(15)
B(22)-B(21)-B(27)	59.3(2)	B(26)-B(21)-B(27)	60.0(2)
C(21)-B(22)-B(21)	58.2(1)	C(21)-B(22)-H(22)	117.0(17)
B(21)-B(22)-H(22)	119.0(17)	C(21)-B(22)-B(23)	58.7(1)
B(21)-B(22)-B(23)	107.3(2)	H(22)-B(22)-B(23)	119.2(17)
C(21)-B(22)-B(27)	105.2(2)	B(21)-B(22)-B(27)	60.5(2)
H(22)-B(22)-B(27)	128.0(17)	B(23)-B(22)-B(27)	108.0(2)
C(21)-B(22)-B(28)	105.0(2)	B(21)-B(22)-B(28)	108.8(2)
H(22)-B(22)-B(28)	127.8(17)	B(23)-B(22)-B(28)	59.4(2)
B(27)-B(22)-B(28)	60.9(2)	C(21)-B(23)-C(22)	60.3(1)
C(21)-B(23)-B(22)	58.6(1)	C(22)-B(23)-B(22)	107.0(2)
C(21)-B(23)-H(23)	117.0(14)	C(22)-B(23)-H(23)	117.9(14)
B(22)-B(23)-H(23)	123.0(14)	C(21)-B(23)-B(24)	106.0(2)
C(22)-B(23)-B(24)	57.9(1)	B(22)-B(23)-B(24)	107.4(2)
H(23)-B(23)-B(24)	125.4(14)	C(21)-B(23)-B(28)	105.2(2)
C(22)-B(23)-B(28)	105.1(2)	B(22)-B(23)-B(28)	59.7(2)
H(23)-B(23)-B(28)	130.3(15)	B(24)-B(23)-B(28)	59.5(2)
C(22)-B(24)-B(23)	59.8(1)	C(22)-B(24)-H(24)	114.3(15)
B(23)-B(24)-H(24)	117.7(15)	C(22)-B(24)-B(25)	58.5(1)
B(23)-B(24)-B(25)	107.7(2)	H(24)-B(24)-B(25)	119.2(15)
C(22)-B(24)-B(28)	106.7(2)	B(23)-B(24)-B(28)	59.6(2)
H(24)-B(24)-B(28)	128.1(15)	B(25)-B(24)-B(28)	108.7(2)
C(22)-B(24)-B(29)	106.1(2)	B(23)-B(24)-B(29)	107.8(2)
H(24)-B(24)-B(29)	129.7(14)	B(25)-B(24)-B(29)	60.5(2)
B(28)-B(24)-B(29)	60.4(2)	C(22)-B(25)-B(20)	59.3(1)
C(22)-B(25)-B(24)	58.9(1)	B(20)-B(25)-B(24)	107.3(2)
C(22)-B(25)-H(25)	118.3(15)	B(20)-B(25)-H(25)	119.7(15)
B(24)-B(25)-H(25)	120.8(15)	C(22)-B(25)-B(26)	106.1(2)
B(20)-B(25)-B(26)	59.6(2)	B(24)-B(25)-B(26)	107.8(2)
H(25)-B(25)-B(26)	125.8(15)	C(22)-B(25)-B(29)	105.7(2)
B(20)-B(25)-B(29)	107.5(2)	B(24)-B(25)-B(29)	59.5(2)
H(25)-B(25)-B(29)	126.8(15)	B(26)-B(25)-B(29)	60.3(2)
B(20)-B(26)-B(21)	60.2(2)	B(20)-B(26)-B(25)	60.4(2)
B(21)-B(26)-B(25)	108.9(2)	B(20)-B(26)-H(26)	117.8(15)
B(21)-B(26)-H(26)	119.7(14)	B(25)-B(26)-H(26)	120.3(15)
B(20)-B(26)-B(27)	108.0(2)	B(21)-B(26)-B(27)	60.2(2)
B(25)-B(26)-B(27)	107.9(2)	H(26)-B(26)-B(27)	124.9(15)
B(20)-B(26)-B(29)	107.8(2)	B(21)-B(26)-B(29)	107.9(2)
B(25)-B(26)-B(29)	59.9(2)	H(26)-B(26)-B(29)	125.4(14)
B(27)-B(26)-B(29)	59.4(2)	B(21)-B(27)-B(22)	60.2(2)
B(21)-B(27)-B(26)	59.8(2)	B(22)-B(27)-B(26)	108.1(2)
B(21)-B(27)-H(27)	117.5(16)	B(22)-B(27)-H(27)	120.4(17)
B(26)-B(27)-H(27)	120.0(16)	B(21)-B(27)-B(28)	107.7(2)
B(22)-B(27)-B(28)	59.8(2)	B(26)-B(27)-B(28)	107.9(2)
H(27)-B(27)-B(28)	125.7(16)	B(21)-B(27)-B(29)	108.6(2)
B(22)-B(27)-B(29)	108.4(2)	B(26)-B(27)-B(29)	60.6(2)
H(27)-B(27)-B(29)	124.4(16)	B(28)-B(27)-B(29)	59.8(2)
B(22)-B(28)-B(23)	60.8(2)	B(22)-B(28)-B(24)	109.4(2)
B(23)-B(28)-B(24)	60.9(2)	B(22)-B(28)-B(27)	59.3(2)
B(23)-B(28)-B(27)	107.8(2)	B(24)-B(28)-B(27)	107.7(2)
B(22)-B(28)-H(28)	121.3(14)	B(23)-B(28)-H(28)	124.1(15)
B(24)-B(28)-H(28)	122.8(14)	B(27)-B(28)-H(28)	119.5(15)
B(22)-B(28)-B(29)	107.7(2)	B(23)-B(28)-B(29)	108.4(2)
B(24)-B(28)-B(29)	59.9(2)	B(27)-B(28)-B(29)	59.5(2)
H(28)-B(28)-B(29)	120.1(15)	B(24)-B(29)-B(25)	60.0(2)
B(24)-B(29)-B(26)	107.7(2)	B(25)-B(29)-B(26)	59.8(2)
B(24)-B(29)-B(27)	108.5(2)	B(25)-B(29)-B(27)	108.2(2)
B(26)-B(29)-B(27)	59.9(2)	B(24)-B(29)-B(28)	59.7(2)

Triethylamine salt of 1-phenyl-2-mercapto-1,2-dicarba-*closo*-dodecaborane

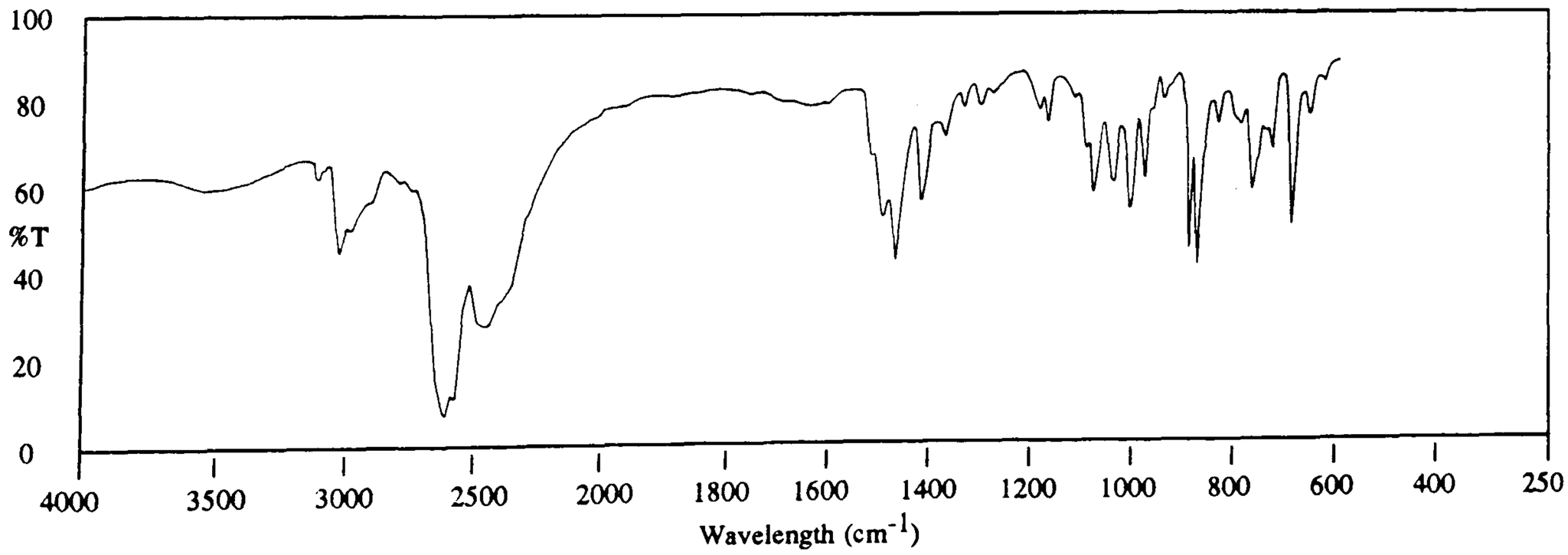


A solution of 0.126g (0.005 moles) 1-phenyl-2-mercapto-*ortho*-carborane in 10ml hexane was treated with 4 drops of dry triethylamine which slowly produced a white precipitate. After 30 minutes the solid was filtered off, washed with fresh hexane and dried *in vacuo* to give 0.13g (73.7%) of triethylamine salt of 1-phenyl-2-mercapto-*ortho*-carborane.

Melting point = 107-109°C (lit[19]. = 109-110°C)

Analysis Found: C,48.2; H,8.9; N,3.7; B,30.6; S,9.1. $C_{14}H_{31}B_{10}NS$ requires C,48.4; H,8.9; N,4.0; B,31.1; S,9.0.

Infrared (KBr disc; cm^{-1}) 3103(w), 3083(w), 3063(w), 3059(w), 3037(w), 2982(m), 2971(m), 2941(m), 2927(m), 2893(w), 2870(w), 2853(w), 2782(w), 2765(w), 2745(w), 2718(w), 2708(w), 2650-2000(m,br), 2619(s), 2609(s), 2592(s), 2581(s), 2567(s), 2545(s), 1578(w), 1495(w), 1472(m), 1447(s), 1398(m), 1389(w), 1370(w), 1351(w), 1318(w), 1283(w), 1260(w), 1246(w), 1194(w), 1182(w), 1175(w), 1158(w), 1110(w), 1087(w), 1072(m), 1064(w), 1038(w), 1033(w), 1002(m), 975(w), 959(w), 939(w), 928(w), 889(s), 874(s), 864(w), 844(w), 835(w), 821(w), 804(w), 792(w), 770(m), 762(w), 746(w), 731(w), 693(m), 671(w), 659(w), 632(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 254 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{32}S$, accompanied by the usual carborane isotope distribution pattern between m/e 248 and 254 and superimposed on a single peak of m/e 101 corresponding to triethylamine, $^{12}C_6{}^{1}H_{15}{}^{14}N$.

^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

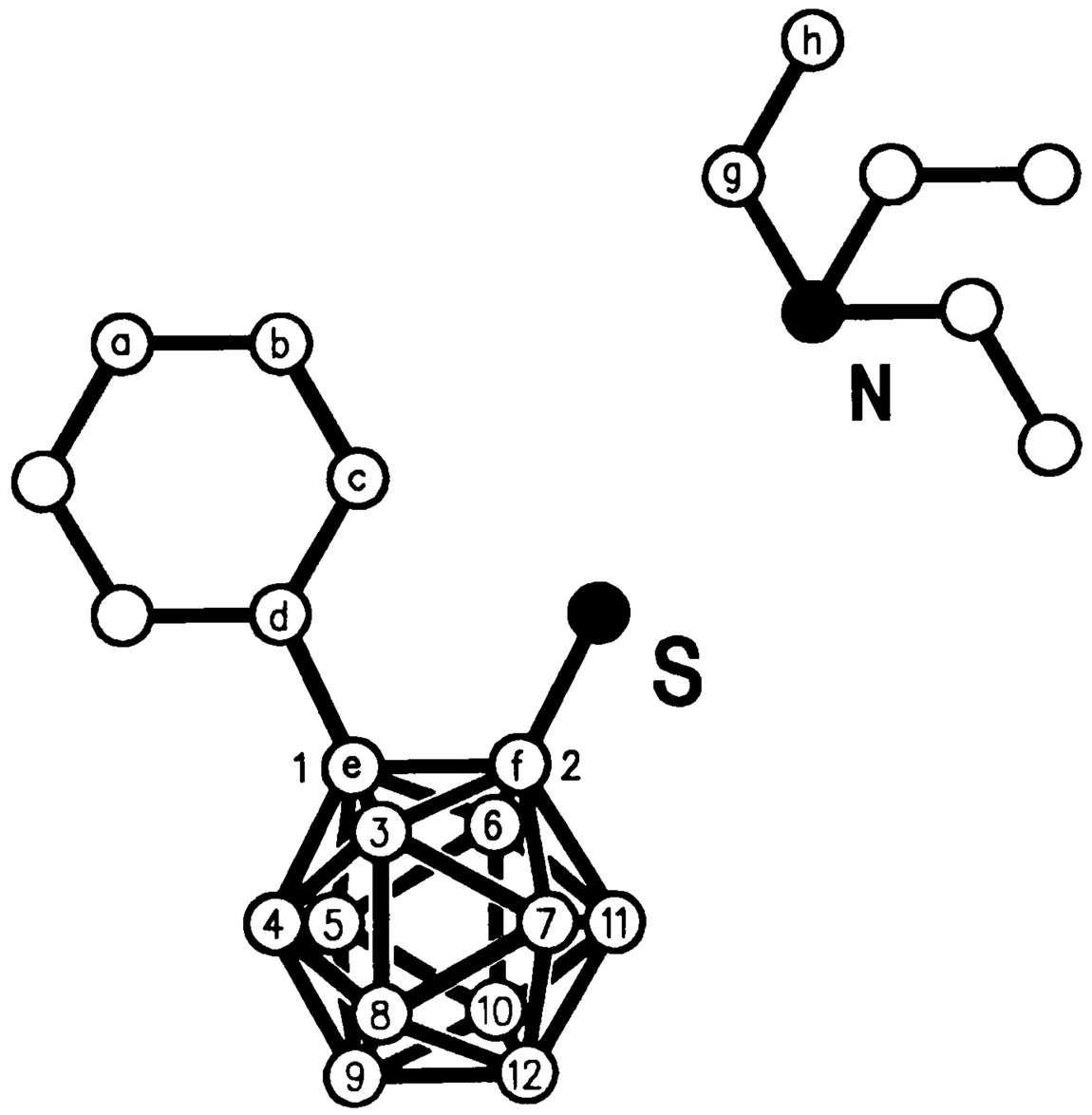
δ_{ppm}	intensity	type of peak	position of proton
7.76-7.74 7.38-7.37	5	multiplet	aromatic C(a,b,c)-H
2.97 2.94 2.91 2.88	6	quartet	ethyl C(g)-H
1.27 1.24 1.21	9	triplet	ethyl C(h)-H
4.1-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent C_6D_6, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

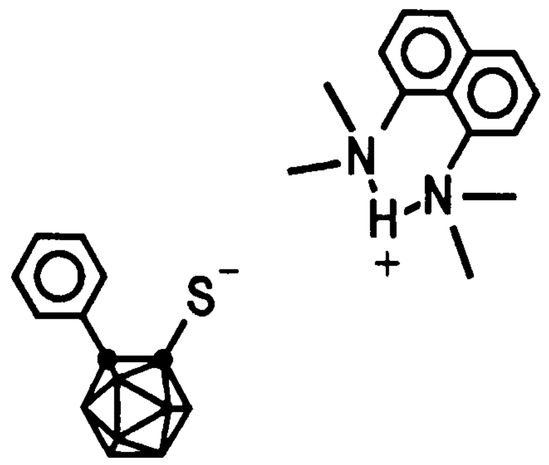
δ_{ppm}	intensity	position of boron
-4.37	1	12
-7.13	2	3,6
-9.70	4	4,5,7,11
-11.64	3	8,10,9

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
133.43	d
131.89	b
129.36	a
127.84	c
100.26	f
88.65	e
45.55	g
8.38	h



Proton sponge salt of 1-phenyl-2-mercapto-1,2-dicarba-*closo*-dodecaborane

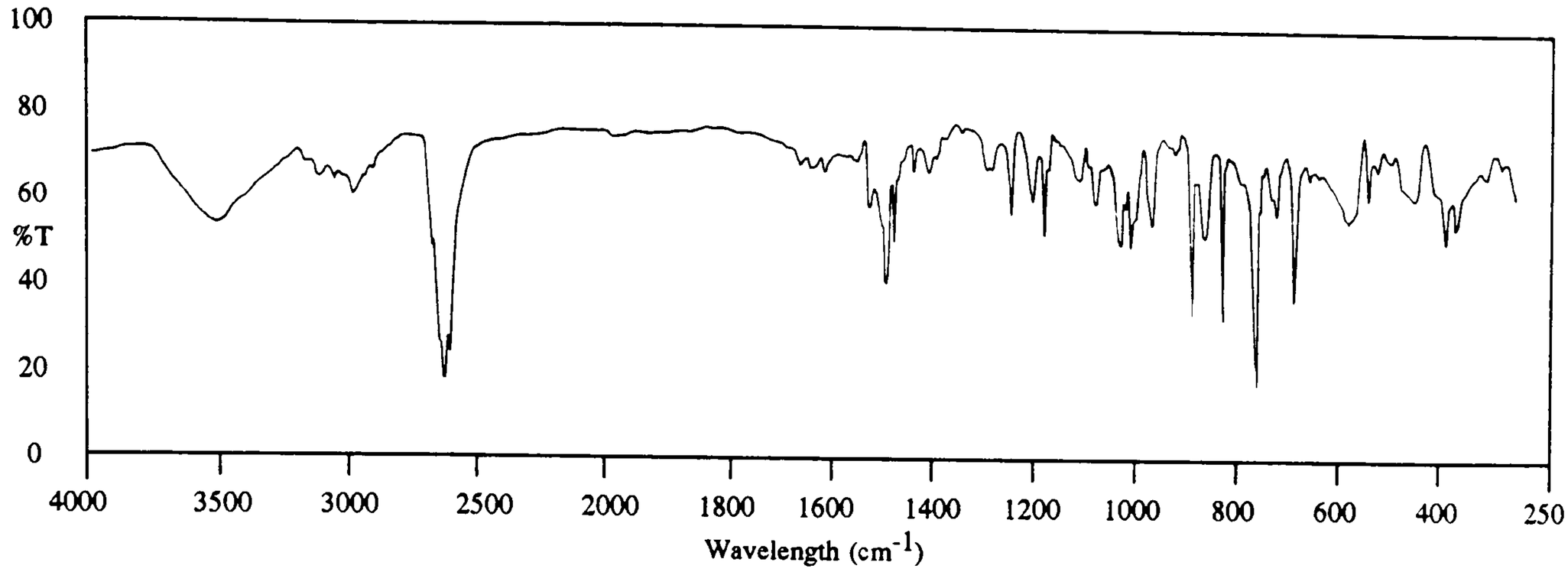


A solution of 0.252g (0.01 moles) 1-phenyl-2-mercapto-*ortho*-carborane in 15ml hexane was added to a solution of 0.214g (0.01 moles) proton sponge in 10ml hexane. An immediate off-white precipitate was formed, filtered off and washed with hexane. The solid was recrystallized from toluene to give 0.38g (81.6%) pale yellow crystals identified as proton sponge salt of 1-phenyl-2-mercapto-*ortho*-carborane.

Melting point = 189-190°C

Analysis Found: C,56.3; H,7.4; N,5.5. $C_{22}H_{34}B_{10}N_2S$ requires C,56.7; H,7.3; N,6.0.

Infrared (KBr disc; cm^{-1}) 3680-3120(m,br), 3114(w), 3062(w), 3047(w), 3008(w), 3000(w), 2984(w), 2971(w), 2964(w), 2932(w), 2891(w), 2855(w), 2819(w), 2640(m), 2604(s), 2588(s), 2566(s), 1628(w), 1607(w), 1601(w), 1582(w), 1521(w), 1499(w), 1474(w), 1468(m), 1451(m), 1443(w), 1434(w), 1413(w), 1383(w), 1370(w), 1352(w), 1320(w), 1277(w), 1266(w), 1230(w), 1207(w), 1189(w), 1168(m), 1164(w), 1110(w), 1105(w), 1087(w), 1074(w), 1020(w), 1010(m), 1003(w), 996(w), 969(m), 936(w), 924(w), 920(w), 893(m), 871(m), 838(m), 830(w), 802(w), 775(s), 771(s), 766(w), 760(w), 743(w), 731(w), 699(m), 670(w), 652(w), 632(w), 605(w), 595(w), 587(w), 572(w), 558(w), 540(w), 517(w), 491(w), 478(w), 470(w), 430(w), 409(m), 391(w), 331(w), 300(w).



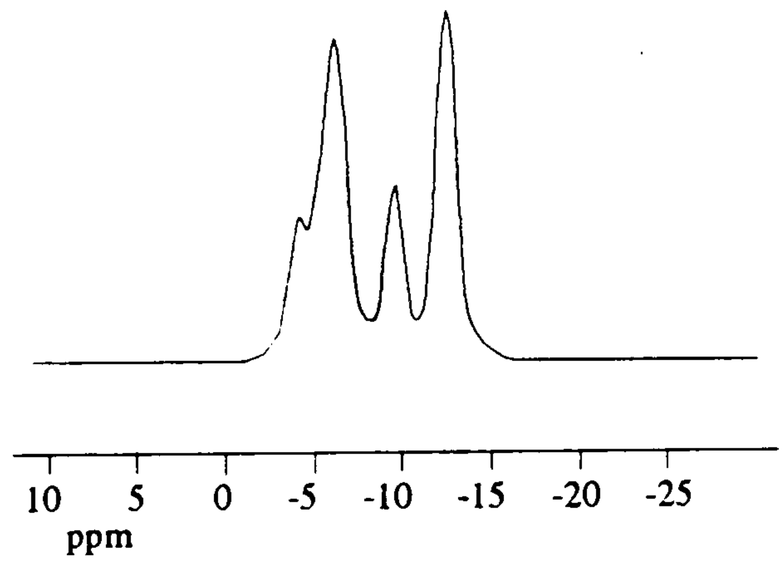
Mass spectrum (E.I.) A highest mass peak was observed at m/e 254 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{32}S$, accompanied by the usual carborane isotope distribution pattern between m/e 248 and 254 and superimposed on a peak of m/e 214 corresponding to proton sponge, $^{12}C_{14}{}^{1}H_{18}{}^{14}N_2$.

^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2SO$ referenced to 2.50ppm.

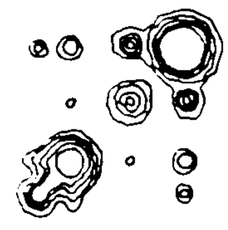
δ_{ppm}	intensity	type of peak	position of proton
8.11-7.38	11	multiplet	aromatic C-H
7.05	1	broad singlet	N-H
3.13	12	singlet	methyl C-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2SO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-4.30	2	3,6
-5.95	3	4,5,12
-9.65	2	7,11
-11.99	3	9,8,10

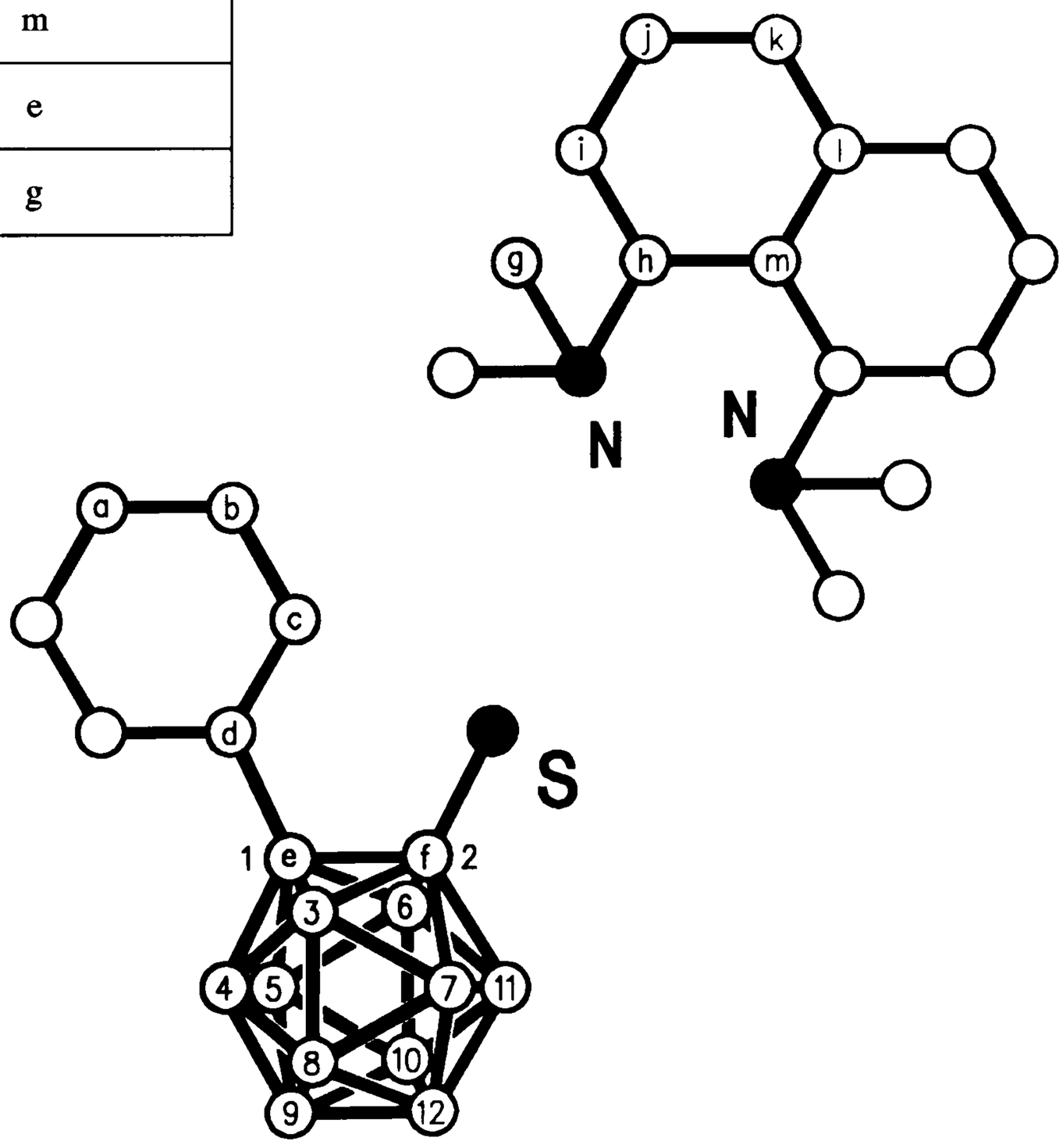


2D COSY



^{13}C N.M.R. solid state M.A.S. 75.431 MHz; referenced externally to $(CH_3)_4Si$ at 0.00ppm.

δ_{ppm}	position of carbon
144.49	h
134.75	l
133.98	f
131.69	d
131.36	j
128.79	b
127.55	a,c
126.84	k
121.68	i
118.90	m
91.84	e
45.72	g



X-ray Analysis (W. Clegg, Newcastle University)

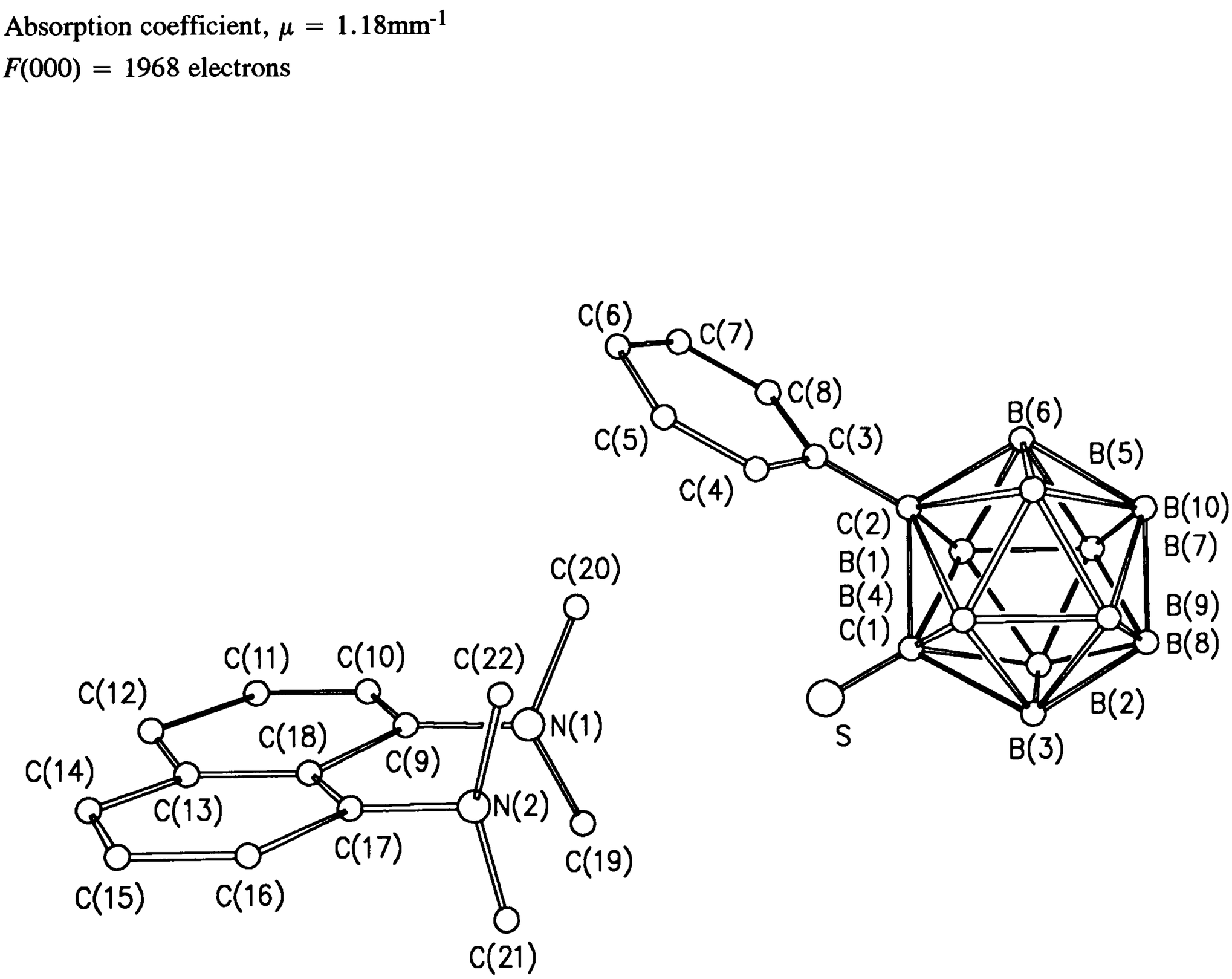
Crystallographic data, CuK_α radiation

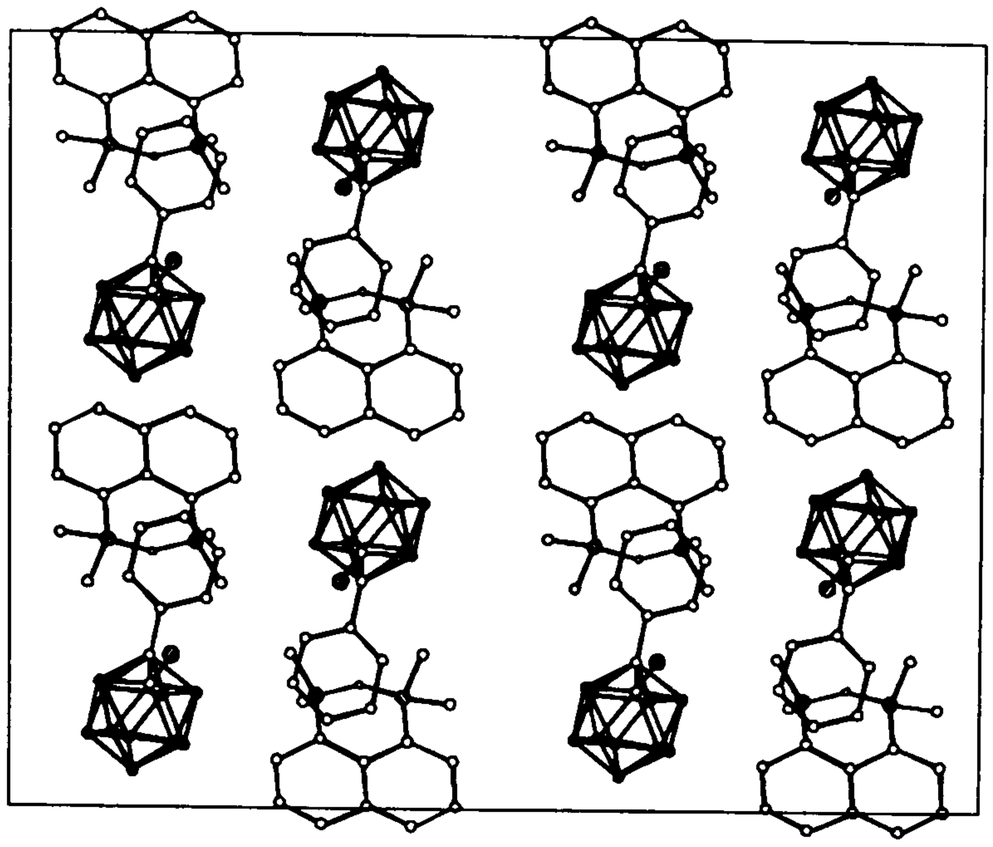
Formula = $C_{22}H_{34}B_{10}N_2S$
Formula weight, M_r = 466.7
System = monoclinic
Space Group = I2/a
(non-standard setting of C2/c)
a = 20.103(6)Å
b = 9.611(3)Å
c = 26.370(8)Å
α = 90°
β = 90.17(3)°
γ = 90°
Unit cell volume, V = 5094.9Å^3
Calculated density, D_c = 1.217gcm^{-3}
Number of formulae per unit cell, Z = 8
Absorption coefficient, μ = 1.18mm^{-1}
F(000) = 1968 electrons

Number of unique reflections = 3166
Observed reflections, $F > 4\sigma_c(F)$ = 2114
$2\theta_{max}$ = 110°
Range, 2θ = 25 to 35°

Range, h = -21 to 21
Range, k = 0 to 10
Range, l = 0 to 28

Measure of overall precision of data, R_{sigma} = 0.029
Crystal size = 0.08 x 0.12 x 0.24mm
Crystal colour = colourless
Temperature, T = 125°K





Bond lengths (Å)

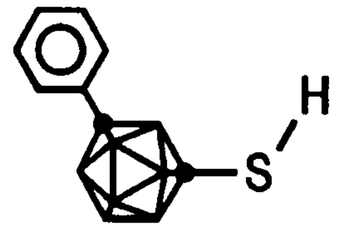
S-C(1)	1.729(4)		C(1)-C(2)	1.835(5)
C(1)-B(1)	1.749(6)		C(1)-B(2)	1.704(6)
C(1)-B(3)	1.695(5)		C(1)-B(4)	1.742(6)
C(2)-C(3)	1.495(5)		C(2)-B(1)	1.725(6)
C(2)-B(4)	1.723(6)		C(2)-B(5)	1.713(6)
C(2)-B(6)	1.694(6)		C(3)-C(4)	1.390(5)
C(3)-C(8)	1.388(5)		C(4)-C(5)	1.389(5)
C(5)-C(6)	1.382(6)		C(6)-C(7)	1.384(6)
C(7)-C(8)	1.388(6)		B(1)-H(1)	1.113(38)
B(1)-B(2)	1.760(6)		B(1)-B(6)	1.793(6)
B(1)-B(7)	1.768(6)		B(2)-H(2)	1.106(39)
B(2)-B(3)	1.772(6)		B(2)-B(7)	1.777(7)
B(2)-B(8)	1.776(6)		B(3)-H(3)	1.139(39)
B(3)-B(4)	1.759(6)		B(3)-B(8)	1.785(6)
B(3)-B(9)	1.784(7)		B(4)-H(4)	1.070(38)
B(4)-B(5)	1.793(6)		B(4)-B(9)	1.773(6)
B(5)-H(5)	1.103(40)		B(5)-B(6)	1.777(6)
B(5)-B(9)	1.772(6)		B(5)-B(10)	1.775(6)
B(6)-H(6)	1.071(39)		B(6)-B(7)	1.757(6)
B(6)-B(10)	1.778(6)		B(7)-H(7)	1.078(41)
B(7)-B(8)	1.789(6)		B(7)-B(10)	1.782(7)
B(8)-H(8)	1.105(39)		B(8)-B(9)	1.789(6)
B(8)-B(10)	1.782(7)		B(9)-H(9)	1.071(39)
B(9)-B(10)	1.781(6)		B(10)-H(10)	1.186(40)
N(1)-H(23)	1.353(49)		N(1)-C(9)	1.473(5)
N(1)-C(19)	1.479(5)		N(1)-C(20)	1.470(5)
N(2)-H(23)	1.267(48)		N(2)-C(17)	1.467(5)
N(2)-C(21)	1.482(5)		N(2)-C(22)	1.483(5)
C(9)-C(10)	1.357(5)		C(9)-C(18)	1.423(5)
C(10)-C(11)	1.408(5)		C(11)-C(12)	1.366(5)
C(12)-C(13)	1.415(5)		C(13)-C(14)	1.407(5)
C(13)-C(18)	1.427(5)		C(14)-C(15)	1.370(6)
C(15)-C(16)	1.401(5)		C(16)-C(17)	1.369(5)
C(17)-C(18)	1.424(5)			

Bond angles (°)

S-C(1)-C(2)	119.8(2)		S-C(1)-B(1)	119.8(3)
C(2)-C(1)-B(1)	57.5(2)		S-C(1)-B(2)	124.6(3)
C(2)-C(1)-B(2)	105.9(3)		B(1)-C(1)-B(2)	61.3(2)
S-C(1)-B(3)	123.8(3)		C(2)-C(1)-B(3)	106.3(3)
B(1)-C(1)-B(3)	111.2(3)		B(2)-C(1)-B(3)	62.9(2)
S-C(1)-B(4)	119.2(3)		C(2)-C(1)-B(4)	57.5(2)
B(1)-C(1)-B(4)	106.8(3)		B(2)-C(1)-B(4)	110.8(3)
B(3)-C(1)-B(4)	61.5(2)		C(1)-C(2)-C(3)	118.9(3)
C(1)-C(2)-B(1)	58.8(2)		C(3)-C(2)-B(1)	119.0(3)
C(1)-C(2)-B(4)	58.6(2)		C(3)-C(2)-B(4)	118.5(3)
B(1)-C(2)-B(4)	108.7(3)		C(1)-C(2)-B(5)	109.8(3)
C(3)-C(2)-B(5)	121.1(3)		B(1)-C(2)-B(5)	113.5(3)
B(4)-C(2)-B(5)	62.9(2)		C(1)-C(2)-B(6)	109.9(3)
C(3)-C(2)-B(6)	121.8(3)		B(1)-C(2)-B(6)	63.3(2)
B(4)-C(2)-B(6)	113.0(3)		B(5)-C(2)-B(6)	62.9(2)
C(2)-C(3)-C(4)	120.9(3)		C(2)-C(3)-C(8)	120.5(3)
C(4)-C(3)-C(8)	118.3(3)		C(3)-C(4)-C(5)	120.7(4)
C(4)-C(5)-C(6)	120.4(4)		C(5)-C(6)-C(7)	119.4(4)
C(6)-C(7)-C(8)	120.0(4)		C(3)-C(8)-C(7)	121.1(4)
C(1)-B(1)-C(2)	63.8(2)		C(1)-B(1)-H(1)	117.0(21)

C(2)-B(1)-H(1)	119.6(20)	C(1)-B(1)-B(2)	58.1(2)
C(2)-B(1)-B(2)	108.3(3)	H(1)-B(1)-B(2)	121.9(20)
C(1)-B(1)-B(6)	109.3(3)	C(2)-B(1)-B(6)	57.5(2)
H(1)-B(1)-B(6)	124.1(21)	B(2)-B(1)-B(6)	108.2(3)
C(1)-B(1)-B(7)	106.8(3)	C(2)-B(1)-B(7)	104.9(3)
H(1)-B(1)-B(7)	127.3(20)	B(2)-B(1)-B(7)	60.5(3)
B(6)-B(1)-B(7)	59.1(3)	C(1)-B(2)-B(1)	60.6(2)
C(1)-B(2)-H(2)	116.4(21)	B(1)-B(2)-H(2)	118.8(20)
C(1)-B(2)-B(3)	58.3(2)	B(1)-B(2)-B(3)	107.1(3)
H(2)-B(2)-B(3)	121.4(20)	C(1)-B(2)-B(7)	108.4(3)
B(1)-B(2)-B(7)	60.0(3)	H(2)-B(2)-B(7)	125.1(21)
B(3)-B(2)-B(7)	108.2(3)	C(1)-B(2)-B(8)	107.5(3)
B(1)-B(2)-B(8)	108.3(3)	H(2)-B(2)-B(8)	126.6(20)
B(3)-B(2)-B(8)	60.4(2)	B(7)-B(2)-B(8)	60.5(3)
C(1)-B(3)-B(2)	58.8(2)	C(1)-B(3)-H(3)	111.6(20)
B(2)-B(3)-H(3)	124.4(20)	C(1)-B(3)-B(4)	60.6(2)
B(2)-B(3)-B(4)	106.9(3)	H(3)-B(3)-B(4)	112.8(19)
C(1)-B(3)-B(8)	107.5(3)	B(2)-B(3)-B(8)	59.9(3)
H(3)-B(3)-B(8)	133.6(19)	B(4)-B(3)-B(8)	107.6(3)
C(1)-B(3)-B(9)	108.8(3)	B(2)-B(3)-B(9)	107.9(3)
H(3)-B(3)-B(9)	125.0(20)	B(4)-B(3)-B(9)	60.1(2)
B(8)-B(3)-B(9)	60.2(3)	C(1)-B(4)-C(2)	63.9(2)
C(1)-B(4)-B(3)	57.9(2)	C(2)-B(4)-B(3)	108.5(3)
C(1)-B(4)-H(4)	115.2(21)	C(2)-B(4)-H(4)	119.7(20)
B(3)-B(4)-H(4)	120.3(21)	C(1)-B(4)-B(5)	110.4(3)
C(2)-B(4)-B(5)	58.3(2)	B(3)-B(4)-B(5)	109.0(3)
H(4)-B(4)-B(5)	125.1(22)	C(1)-B(4)-B(9)	107.2(3)
C(2)-B(4)-B(9)	105.7(3)	B(3)-B(4)-B(9)	60.7(3)
H(4)-B(4)-B(9)	127.5(20)	B(5)-B(4)-B(9)	59.6(2)
C(2)-B(5)-B(4)	58.8(2)	C(2)-B(5)-H(5)	118.3(20)
B(4)-B(5)-H(5)	120.9(20)	C(2)-B(5)-B(6)	58.1(2)
B(4)-B(5)-B(6)	105.9(3)	H(5)-B(5)-B(6)	120.6(20)
C(2)-B(5)-B(9)	106.2(3)	B(4)-B(5)-B(9)	59.6(2)
H(5)-B(5)-B(9)	126.1(20)	B(6)-B(5)-B(9)	107.9(3)
C(2)-B(5)-B(10)	105.6(3)	B(4)-B(5)-B(10)	106.9(3)
H(5)-B(5)-B(10)	126.6(20)	B(6)-B(5)-B(10)	60.1(2)
B(9)-B(5)-B(10)	60.3(2)	C(2)-B(6)-B(1)	59.2(2)
C(2)-B(6)-B(5)	59.1(2)	B(1)-B(6)-B(5)	107.3(3)
C(2)-B(6)-H(6)	120.9(20)	B(1)-B(6)-H(6)	116.4(21)
B(5)-B(6)-H(6)	126.1(21)	C(2)-B(6)-B(7)	106.7(3)
B(1)-B(6)-B(7)	59.7(3)	B(5)-B(6)-B(7)	108.4(3)
H(6)-B(6)-B(7)	120.0(21)	C(2)-B(6)-B(10)	106.2(3)
B(1)-B(6)-B(10)	107.6(3)	B(5)-B(6)-B(10)	59.9(2)
H(6)-B(6)-B(10)	126.9(21)	B(7)-B(6)-B(10)	60.5(3)
B(1)-B(7)-B(2)	59.6(3)	B(1)-B(7)-B(6)	61.1(3)
B(2)-B(7)-B(6)	109.1(3)	B(1)-B(7)-H(7)	123.0(22)
B(2)-B(7)-H(7)	124.7(23)	B(6)-B(7)-H(7)	118.5(22)
B(1)-B(7)-B(8)	107.3(3)	B(2)-B(7)-B(8)	59.7(3)
B(6)-B(7)-B(8)	108.4(3)	H(7)-B(7)-B(8)	122.6(21)
B(1)-B(7)-B(10)	108.5(3)	B(2)-B(7)-B(10)	108.0(3)
B(6)-B(7)-B(10)	60.3(3)	H(7)-B(7)-B(10)	118.9(23)
B(8)-B(7)-B(10)	59.9(3)	B(2)-B(8)-B(3)	59.7(3)
B(2)-B(8)-B(7)	59.8(3)	B(3)-B(8)-B(7)	107.1(3)
B(2)-B(8)-H(8)	125.7(22)	B(3)-B(8)-H(8)	126.9(21)
B(7)-B(8)-H(8)	119.8(21)	B(2)-B(8)-B(9)	107.5(3)
B(3)-B(8)-B(9)	59.9(3)	B(7)-B(8)-B(9)	107.1(3)
H(8)-B(8)-B(9)	121.1(22)	B(2)-B(8)-B(10)	108.1(3)
B(3)-B(8)-B(10)	107.9(3)	B(7)-B(8)-B(10)	59.9(3)
H(8)-B(8)-B(10)	116.0(22)	B(9)-B(8)-B(10)	59.8(3)
B(3)-B(9)-B(4)	59.3(2)	B(3)-B(9)-B(5)	108.8(3)
B(4)-B(9)-B(5)	60.7(2)	B(3)-B(9)-B(8)	59.9(3)
B(4)-B(9)-B(8)	106.8(3)	B(5)-B(9)-B(8)	108.2(3)
B(3)-B(9)-H(9)	120.6(22)	B(4)-B(9)-H(9)	122.3(21)
B(5)-B(9)-H(9)	122.0(22)	B(8)-B(9)-H(9)	121.6(21)
B(3)-B(9)-B(10)	108.0(3)	B(4)-B(9)-B(10)	107.5(3)
B(5)-B(9)-B(10)	59.9(2)	B(8)-B(9)-B(10)	59.9(3)
H(9)-B(9)-B(10)	122.6(21)	B(5)-B(10)-B(6)	60.0(2)
B(5)-B(10)-B(7)	107.5(3)	B(6)-B(10)-B(7)	59.2(2)
B(5)-B(10)-B(8)	108.4(3)	B(6)-B(10)-B(8)	107.8(3)
B(7)-B(10)-B(8)	60.3(3)	B(5)-B(10)-B(9)	59.8(2)
B(6)-B(10)-B(9)	107.5(3)	B(7)-B(10)-B(9)	107.7(3)
B(8)-B(10)-B(9)	60.3(3)	B(5)-B(10)-H(10)	124.1(20)
B(6)-B(10)-H(10)	118.6(19)	B(7)-B(10)-H(10)	117.4(20)
B(8)-B(10)-H(10)	121.7(19)	B(9)-B(10)-H(10)	126.9(19)
H(23)-N(1)-C(9)	99.3(20)	H(23)-N(1)-C(19)	111.9(20)
C(9)-N(1)-C(19)	111.4(3)	H(23)-N(1)-C(20)	108.3(21)
C(9)-N(1)-C(20)	113.0(3)	C(19)-N(1)-C(20)	112.1(3)
H(23)-N(2)-C(17)	99.6(22)	H(23)-N(2)-C(21)	113.1(22)
C(17)-N(2)-C(21)	112.2(3)	H(23)-N(2)-C(22)	106.8(23)
C(17)-N(2)-C(22)	112.2(3)	C(21)-N(2)-C(22)	112.1(3)
N(1)-H(23)-N(2)	157.5(42)	N(1)-C(9)-C(10)	120.9(3)
N(1)-C(9)-C(18)	117.9(3)	C(10)-C(9)-C(18)	121.1(3)
C(9)-C(10)-C(11)	120.8(4)	C(10)-C(11)-C(12)	120.4(4)
C(11)-C(12)-C(13)	120.1(4)	C(12)-C(13)-C(14)	120.2(3)
C(12)-C(13)-C(18)	120.0(3)	C(14)-C(13)-C(18)	119.8(3)
C(13)-C(14)-C(15)	121.2(4)	C(14)-C(15)-C(16)	119.8(4)
C(15)-C(16)-C(17)	120.5(3)	N(2)-C(17)-C(16)	120.0(3)
N(2)-C(17)-C(18)	118.4(3)	C(16)-C(17)-C(18)	121.6(3)
C(9)-C(18)-C(13)	117.5(3)	C(9)-C(18)-C(17)	125.3(3)
C(13)-C(18)-C(17)	117.2(3)		

1-phenyl-7-mercapto-1,7-dicarba-*closo*-dodecaborane

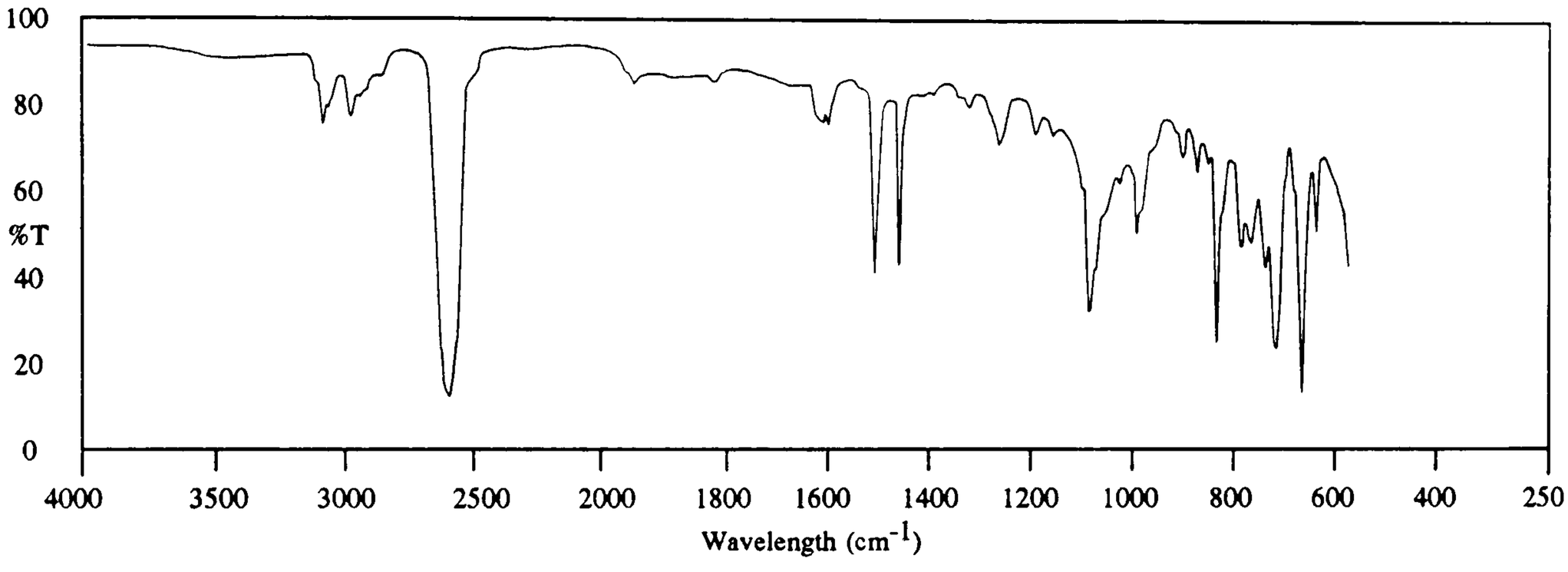


Using a dry ice bath at -40°C, 0.1g iron (III) nitrate nonahydrate and 0.56g (0.02 moles) sodium metal were slowly added to 50ml of liquid ammonia with stirring for 30 minutes. A solution of 2.20g (0.01 moles) 1-phenyl-*meta*-carborane in 20ml hexane and, after one hour, 0.32g (0.01 moles) of powdered sulphur were added to the solution. The mixture was left to evaporate for 8 hours at ambient temperature. 10ml of ethanol and 50ml of water were added to the solid residue and the organic solvents were pumped off using a rotary evaporator. The blue-black aqueous layer was filtered with activated charcoal, acidified with dilute hydrochloric acid and the products were extracted with hexane. The combined hexane extracts were washed with 10% potassium bicarbonate solution, dried over anhydrous magnesium sulphate and filtered. The organic solvent was removed by rotary evaporator to give an oily residue which was vacuum distilled at 100°C and 0.05mmHg to give 1.97g (78.2%) of 1-phenyl-7-mercapto-*meta*-carborane.

Melting point = 43-44°C

Analysis Found: C,37.8; H,6.5; B,42.2; S,12.7. $C_8H_{16}B_{10}S$ requires C,38.1; H,6.4; B,42.9; S,12.7.

Infrared (neat; cm^{-1}) 3084(w), 3060(w), 3038(w), 3022(w), 3012(w), 2948(w), 2916(w), 2843(w), 2604(s), 2592(s), 2563(s), 1974(w), 1958(w), 1885(w), 1808(w), 1604(w), 1593(w), 1582(w), 1579(w), 1530(w), 1496(m), 1491(m), 1449(m), 1443(w), 1433(w), 1389(w), 1340(w), 1332(w), 1318(w), 1283(w), 1260(w), 1252(w), 1193(w), 1162(w), 1108(w), 1090(m), 1081(m), 1068(w), 1063(w), 1034(w), 1003(m), 996(w), 992(w), 973(w), 951(w), 931(w), 919(w), 890(w), 867(w), 852(s), 840(w), 808(m), 790(m), 757(m), 740(s), 732(s), 719(w), 702(w), 691(s), 660(m), 577(m).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 254 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{32}S$, accompanied by the usual carborane isotope distribution pattern between m/e 248 and 254.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

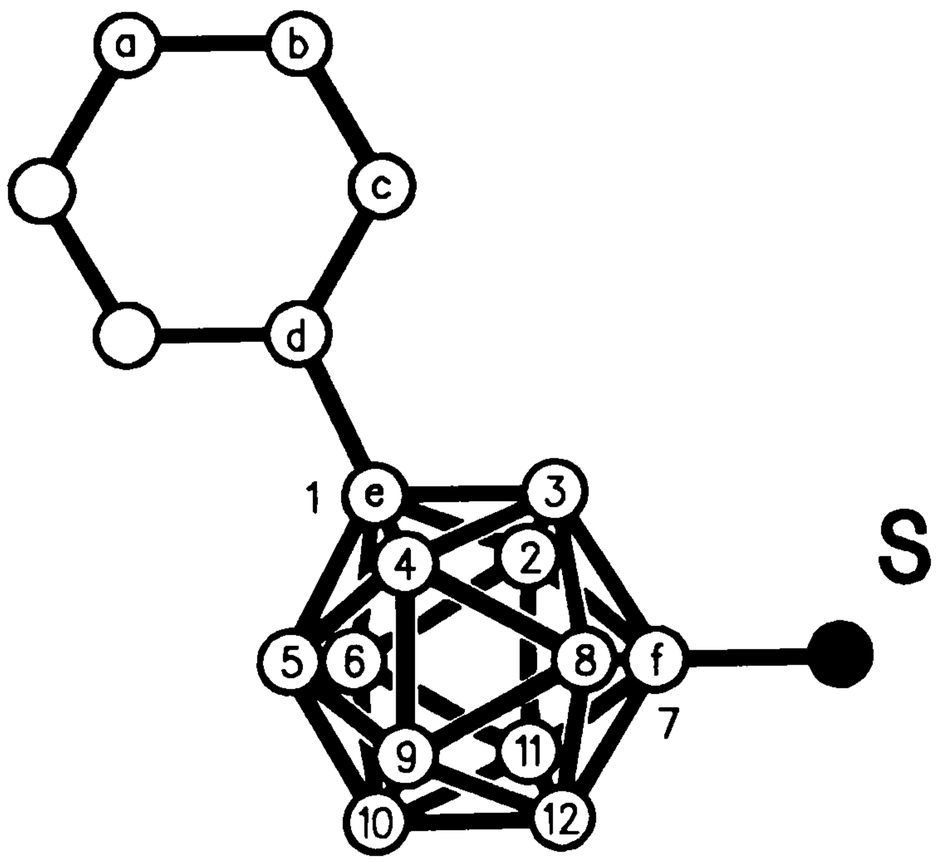
δ_{ppm}	intensity	type of peak	position of proton
7.52-7.24	5	multiplet	aromatic C-H
3.48	1	singlet	S-H
4.2-1.3	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

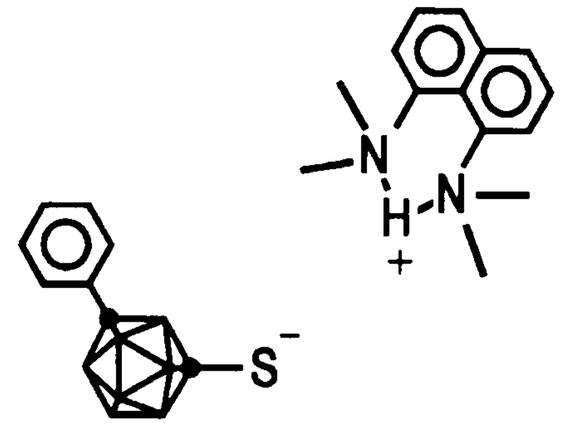
δ_{ppm}	intensity	position of boron
-3.49	1	5
-7.07	1	12
-9.43	6	4,6,9,10,8,11
-11.41	2	2,3

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
134.58	d
128.90	b
128.44	a
127.70	c
79.48	e
74.29	f



Proton sponge adduct of 1-phenyl-7-mercapto-1,7-dicarba-*closo*-dodecaborane

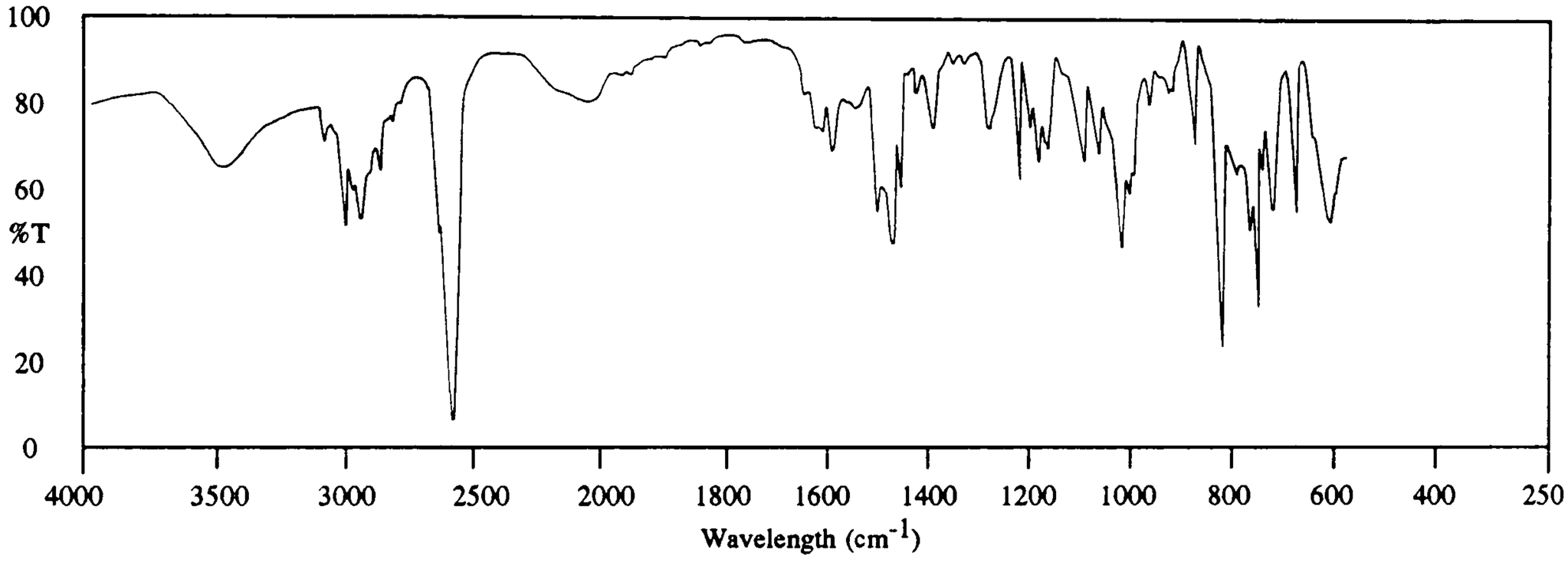


0.252g (0.001 moles) of 1-phenyl-7-mercapto-*meta*-carborane in 15ml of hexane was added to a solution of 0.214g (0.001 moles) proton sponge in 10ml hexane. A yellow precipitate appeared after 30 minutes which was filtered off and washed with hexane to give 0.43g (92.3%) 1:1 proton sponge : 1-phenyl-7-mercapto-*meta*-carborane adduct. The solid was insoluble in all solvents tried, including toluene, chloroform, methanol and dimethylsulphoxide.

Melting point = 120-121°C

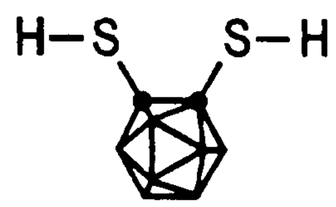
Analysis Found: C,56.2; H,7.3; B,22.8; S,6.8. $C_{22}H_{34}B_{10}N_2S$ requires C,56.7; H,7.3; B,23.2; S,6.9.

Infrared (KBr disc; cm^{-1}) 3626(w), 3600-3120(w,br), 3083(w), 3054(w), 3015(w), 2980(w), 2949(w), 2923(w), 2884(w), 2845(w), 2798(w), 2764(w), 2632(m), 2600(s), 2568(s), 1622(w), 1602(w), 1592(w), 1573(w), 1543(w), 1534(w), 1530(w), 1516(w), 1492(m), 1464(m), 1446(m), 1427(w), 1409(w), 1379(w), 1341(w), 1317(w), 1277(w), 1267(w), 1220(m), 1198(w), 1182(m), 1170(m), 1166(m), 1136(w), 1099(m), 1072(m), 1048(w), 1030(m), 1017(m), 1007(m), 972(w), 954(w), 946(w), 937(w), 928(w), 916(w), 888(m), 855(w), 843(s), 818(m), 810(m), 787(m), 772(s), 759(m), 742(m), 697(m), 660(m), 632(m), 622(m).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 254 corresponding to the species $^{12}C_8{}^{1}H_{16}{}^{11}B_{10}{}^{32}S$, accompanied by the usual carborane isotope distribution pattern between m/e 248 and 254. A peak of m/e 214 corresponding to the species $^{12}C_{14}{}^{1}H_{18}{}^{14}N_2$ was also present.

1,2-dimercapto-1,2-dicarba-*closo*-dodecaborane

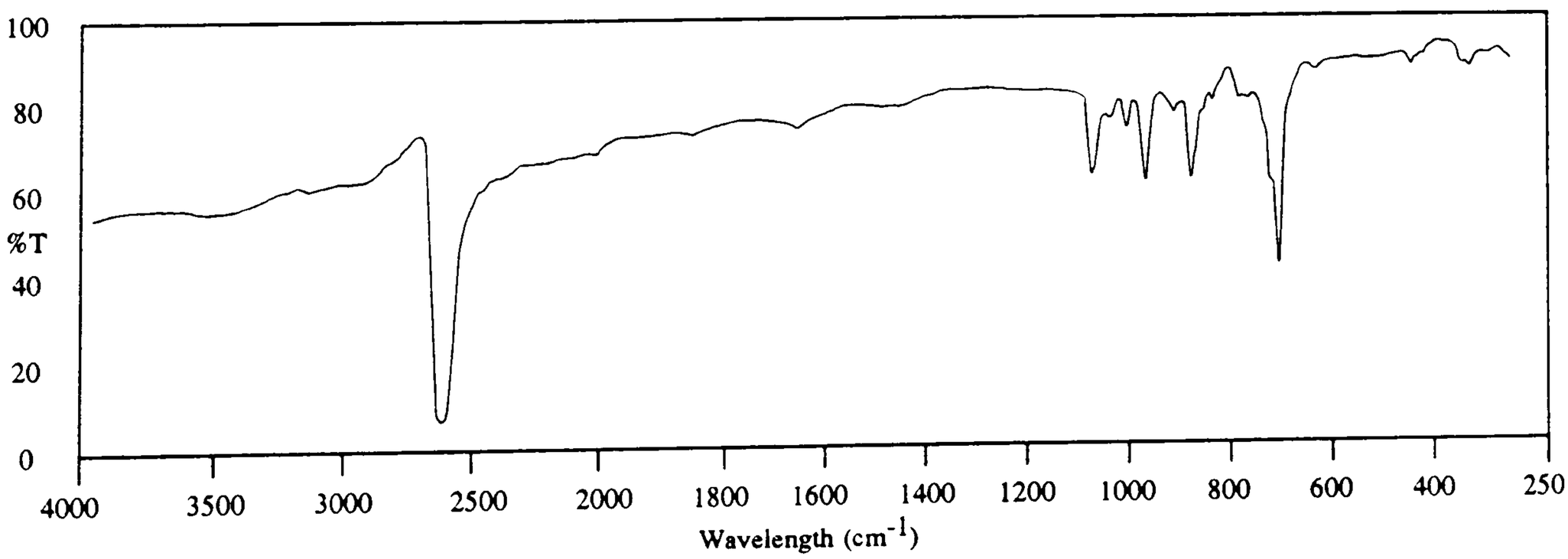


To an ice-cold nitrogen purged 1,2-dilithio-*ortho*-carborane solution, made from 1.44g (0.01 moles) of *ortho*-carborane and 14.2ml (0.02 moles) of *neo*-butyllithium (in hexane, 1.6M) in 50ml of diethyl ether, was added 0.64g (0.02 moles) of sulphur powder in small portions over a 10 minute period. The solution was stirred for an hour and the temperature was allowed to rise to 20°C after 30 minutes. At 0°C, dilute hydrochloric acid was added dropwise to the solution and stirred to 20°C for 15 minutes. The organic layer was separated, dried over anhydrous magnesium sulphate and filtered. The solvents were vacuum-evaporated to leave a solid which was recrystallized from 40-60°C petroleum ether to give 1.52g (73.1%) 1,2-dimercapto-*ortho*-carborane.

Melting point = 258-259°C (lit[17]. = 265-267°C)

Analysis Found: C,11.3; H,5.5. $C_2H_{12}B_{10}S_2$ requires C,11.5; H,5.8.

Infrared (KBr disc; cm^{-1}) 2598(s), 1080(m), 1076(m), 1049(w), 1013(w), 977(m), 922(w), 890(m), 882(w), 871(w), 851(w), 802(w), 797(w), 782(w), 750(w), 738(m), 726(s), 692(w), 656(w), 476(w), 378(w), 364(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 210 corresponding to the species $^{12}C_2{}^{1}H_{12}{}^{11}B_{10}{}^{32}S_2$, accompanied by the usual carborane isotope distribution pattern between m/e 204 and 210.

^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

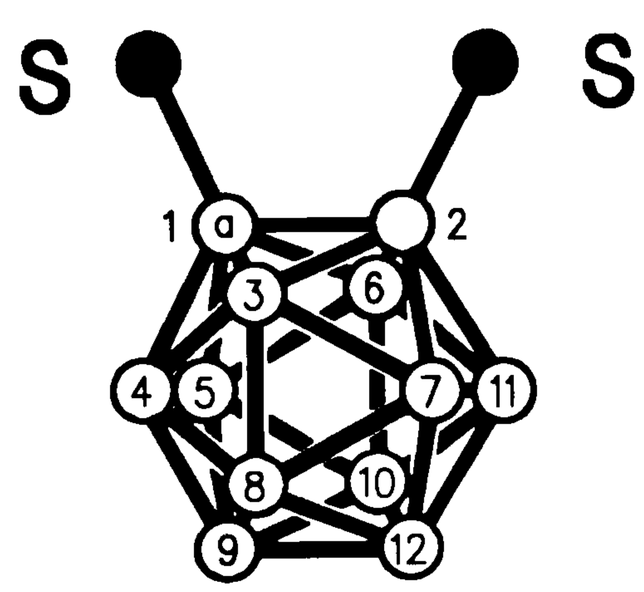
δ_{ppm}	intensity	type of peak	position of proton
2.80	2	singlet	S-H
3.9-0.8	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent C_6D_6, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

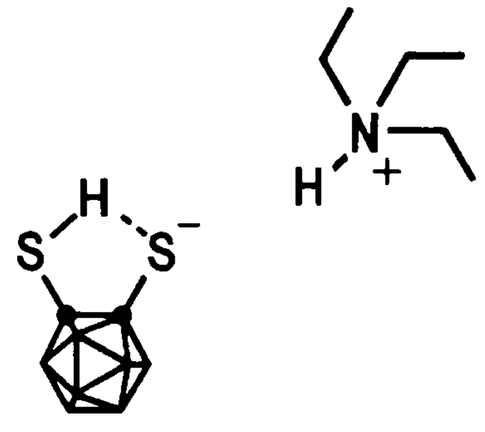
δ_{ppm}	intensity	position of boron
-2.99	2	9,12
-7.17	6	4,5,7,11,8,10
-9.07	2	3,6

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
79.66	a



Triethylamine adduct of 1,2-dimercapto-1,2-dicarba-*closo*-dodecaborane

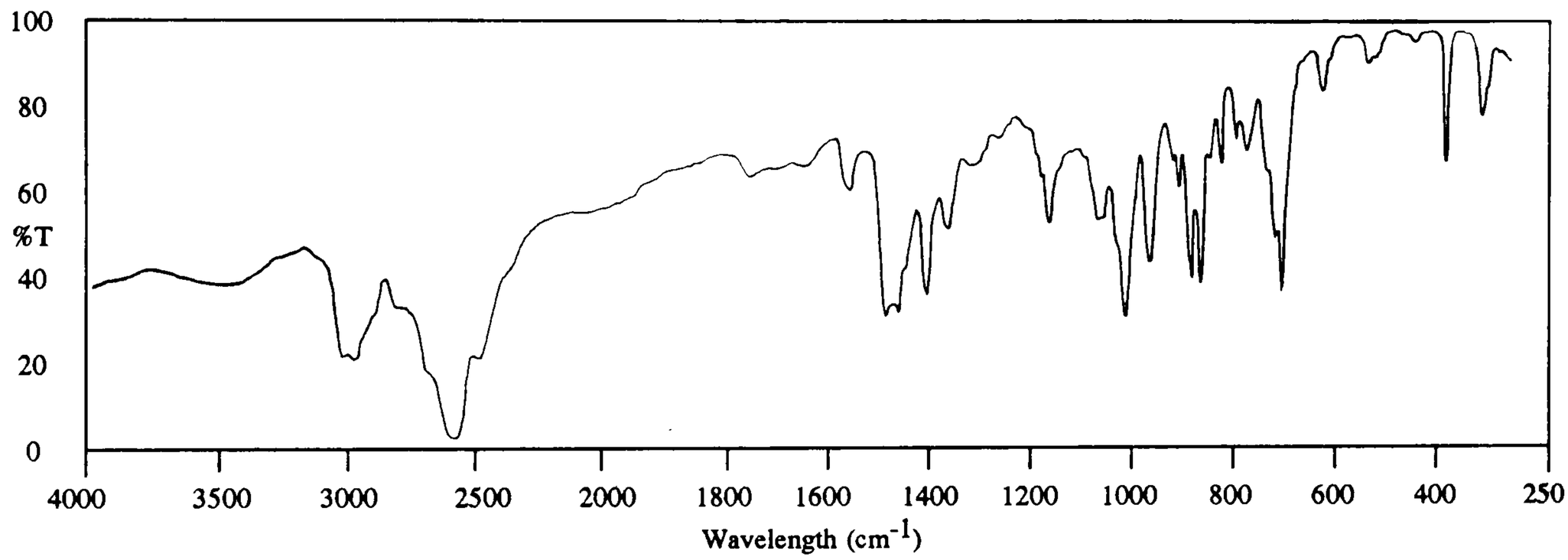


A solution of 0.21g 1,2-dimercapto-*ortho*-carborane in 10ml hexane was treated with six drops of triethylamine slowly affording a gum-like precipitate. The solvents were decanted off leaving a solid which was washed with hexane and dissolved in a 1:1 hexane : toluene mixture. From the solution 0.24g (77.7%) of 1:1 triethylamine : 1,2-dimercapto-*ortho*-carborane adduct was obtained.

Melting point = 182-184°C

Analysis Found: C,31.6; H,8.8; N,4.1; B,33.5. $C_8H_{27}B_{10}NS_2$ requires C,31.1; H,8.7; N,4.5; B,35.0.

Infrared (KBr disc; cm^{-1}) 3022(w), 3004(w), 2995(m), 2975(m), 2956(m), 2943(m), 2937(m), 2909(w), 2884(w), 2875(w), 2810-2320(m,br), 2605(s), 2594(s), 2571(s), 2547(s), 1729(w), 1681(w), 1620(w), 1548(w), 1542(w), 1472(m), 1462(m), 1450(m), 1440(m), 1434(m), 1401(m), 1394(m), 1380(w), 1358(w), 1352(w), 1314(w), 1308(w), 1296(w), 1257(w), 1241(w), 1186(w), 1176(w), 1162(w), 1146(w), 1072(w), 1064(w), 1034(w), 1020(m), 973(m), 930(w), 918(w), 892(m), 876(m), 861(w), 838(w), 811(w), 791(w), 787(w), 752(w), 738(m), 727(m), 701(w), 684(w), 672(w), 648(w), 635(w), 617(w), 560(w), 549(w), 541(w), 538(w), 468(w), 463(w), 412(w), 343(w), 340(w), 337(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 210 corresponding to the species $^{12}C_2{}^{1}H_{12}{}^{11}B_{10}{}^{32}S_2$, accompanied by the usual carborane isotope distribution pattern between m/e 204 and 210. A peak of m/e 101 was present and assigned to triethylamine, $^{12}C_6{}^{1}H_{15}{}^{14}N$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

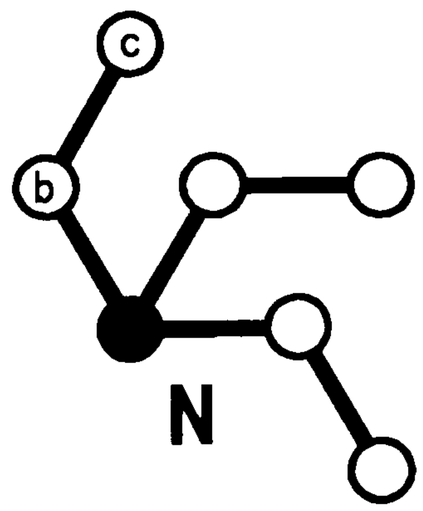
δ_{ppm}	intensity	type of peak	position of proton
6.65	2	broad singlet	S-H, N-H
3.08 3.06 3.05 3.03	6	quartet	ethyl C(b)-H
1.36 1.34 1.32	9	triplet	ethyl C(c)-H

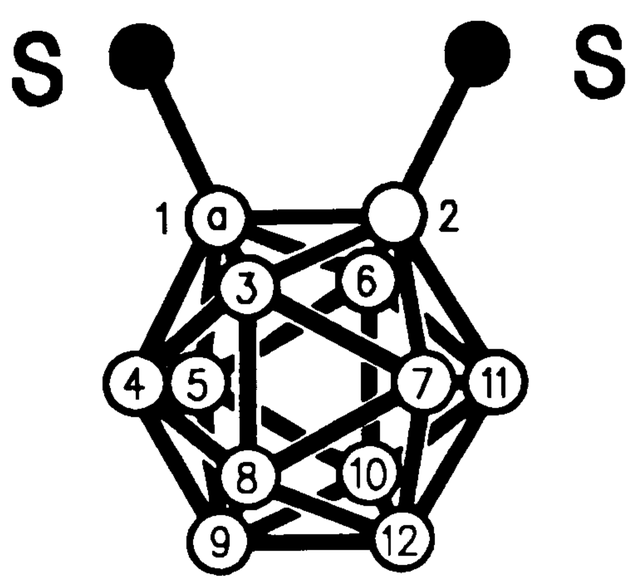
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-4.31	2	9,12
-8.97	6	4,5,7,11,8,10
-11.89	2	3,6

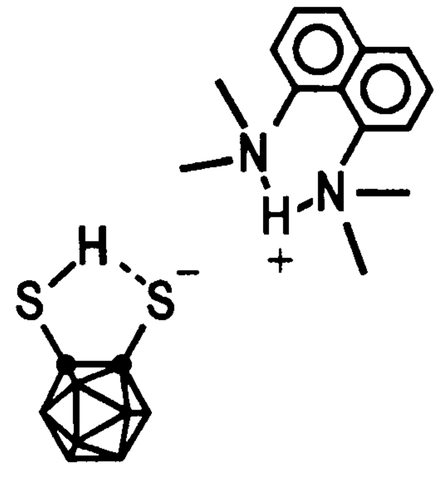
^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
93.34	a
46.69	b
9.23	c





Proton sponge salt of 1,2-dimercapto-1,2-dicarba-*closo*-dodecaborane

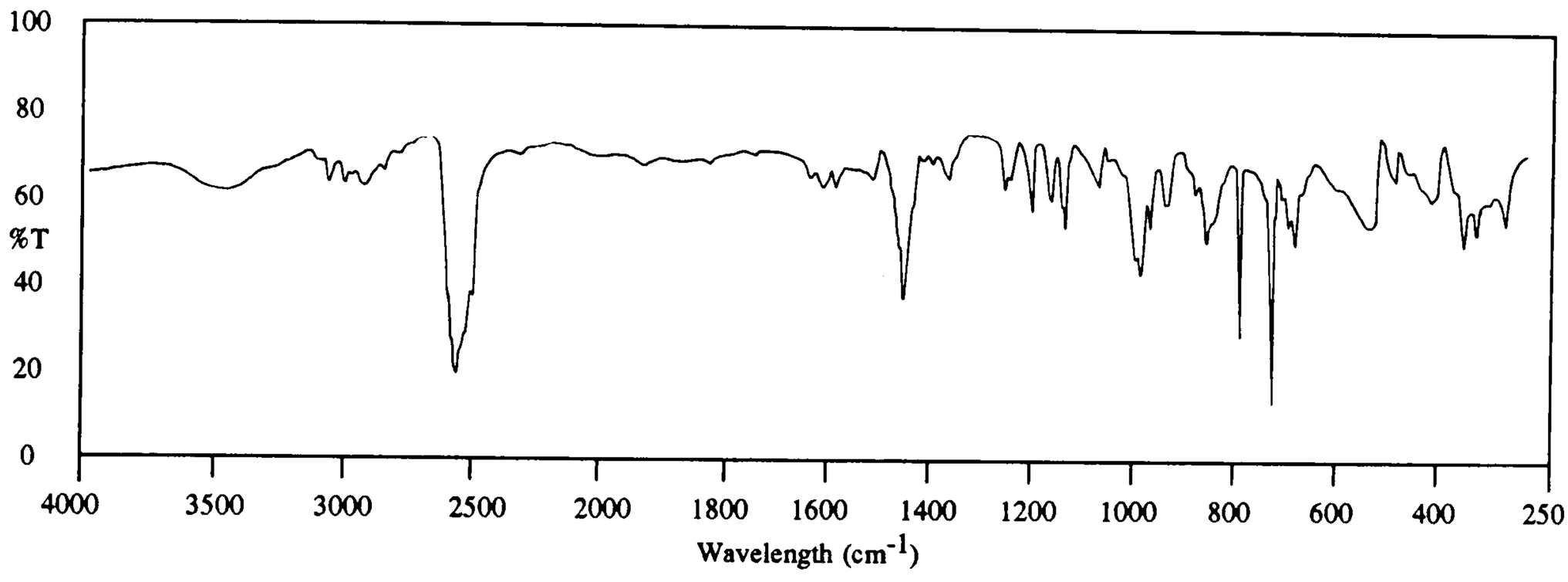


0.21g (0.001 moles) of 1,2-dimercapto-*ortho*-carborane was dissolved in 10ml of hexane which was poured into a solution of 0.22g (0.001 moles) proton sponge in 10ml hexane. The precipitate formed was filtered off, washed with hexane and recrystallized from toluene to give 0.37g (91.2%) proton sponge salt of 1,2-dimercapto-*ortho*-carborane.

Melting point = 157-158°C

Analysis Found: C,45.4; H,7.0; N,6.4; B,25.7; S,15.5. $C_{16}H_{30}B_{10}N_2S_2$ requires C,45.5; H,7.1; N,6.6; B,25.6; S,15.2.

Infrared (KBr disc; cm^{-1}) 3460-3360(w,br), 3102(w), 3088(w), 3056(w), 3037(w), 3000(w), 2965(w), 2937(w), 2924(w), 2889(w), 2853(w), 2798(w), 2609(m), 2601(s), 2582(s), 2563(s), 2552(s), 2521(m), 1628(w), 1604(w), 1581(w), 1573(w), 1518(w), 1472(m), 1465(m), 1450(w), 1447(w), 1428(w), 1410(w), 1389(w), 1378(w), 1273(w), 1264(w), 1233(m), 1188(w), 1168(w), 1162(m), 1139(w), 1131(w), 1102(w), 1083(w), 1053(w), 1031(m), 1021(m), 1002(m), 976(w), 970(w), 931(w), 918(w), 897(m), 887(w), 881(w), 862(w), 832(s), 827(w), 771(s), 766(w), 751(w), 739(w), 727(m), 716(w), 692(w), 645(w), 621(w), 614(w), 608(w), 592(m), 581(m), 578(m), 549(w), 541(w), 538(w), 512(w), 490(w), 484(w), 478(w), 470(w), 461(w), 424(w), 419(w), 408(m), 383(m), 377(w), 358(w), 329(m).



Mass spectrum (F.A.B. in $CHCl_3$) A highest mass peak was observed at m/e 215 corresponding to the proton sponge cation $^{12}C_{14}{}^{1}H_{19}{}^{14}N_2$. It was superimposed on a group of peaks with the usual carborane isotope distribution pattern between m/e 203 and 209 assigned to the anion $^{12}C_2{}^{1}H_{11}{}^{11}B_{10}{}^{32}S_2$.

^{1}H N.M.R. 250.134 MHz; solvent $(CD_3)_2SO$ referenced to 2.50ppm.

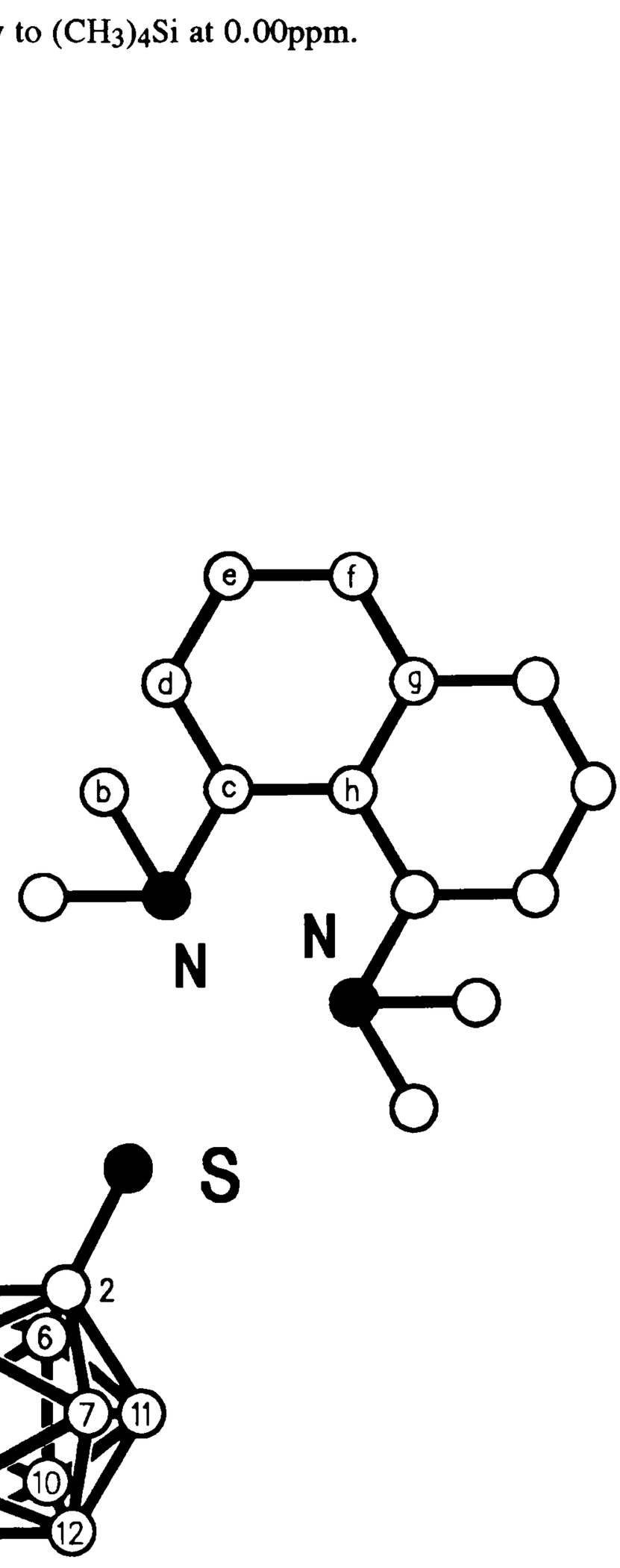
δ_{ppm}	intensity	type of peak	position of proton
8.31	2	broad singlet	S-H
8.09-7.74	6	multiplet	aromatic C-H
3.13	12	singlet	methyl C-H
4.0-1.1	10	multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $(CD_3)_2SO$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

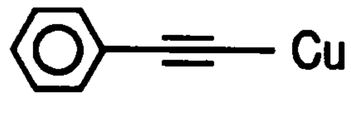
δ_{ppm}	intensity	position of boron
2.11	2	9,12
-4.90	6	4,5,7,11,8,10
-7.25	2	3,6

^{13}C N.M.R. solid state M.A.S. 75.431 MHz; referenced externally to $(CH_3)_4Si$ at 0.00ppm.

δ_{ppm}	position of carbon
144.54	c
134.76	g
130.03	e
126.82	f
121.71	d
118.95	h
96.55	a
45.73	b



Phenylethynyl copper

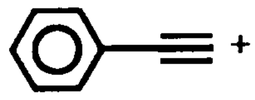


19.05g (0.1 moles) of copper iodide was dissolved in 200ml concentrated aqueous ammonia solution (0.88M) and the deep blue solution was added dropwise to a mechanically stirred solution containing 10.20g (0.1 moles) of phenylacetylene in 500ml absolute alcohol. The solution was stirred for 30 minutes and the heavy yellow precipitate (appears green due to the blue solution) was filtered off and washed with water, ethanol and diethyl ether. The yellow solid was vacuum dried for 2 hours to give 11.4g (69.3%) of phenylethynyl copper.

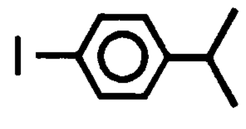
Analysis Found: C,58.1; H,3.1. C_8H_5Cu requires C,58.4; H,3.0.

Infrared (KBr disc; cm^{-1}) 3098(w), 3086(w), 3070(w), 3039(w), 3011(w), 1591(w), 1481(m), 1474(w), 1441(w), 1439(w), 1068(w), 1024(w), 914(w), 902(w), 773(w), 742(s), 738(m), 679(s), 669(w), 520(m), 511(m), 368(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 202 corresponding to the species $^{12}C_{16}{}^{1}H_{10}$ which was probably 1,4-diphenylbutadiyne. A peak observed at m/e 101 was assigned to:



1-iodo-4-(2-propyl)benzene



20ml (0.15 moles) of 4-(2-propyl)aniline was dissolved in 60ml of 1:1 hydrochloric acid : distilled water with stirring and the solution was cooled to 0°C with an ice-salt bath and a solution of 10.35g (0.15 moles) sodium nitrite in 20ml water was added dropwise. After the bath was removed, the solution was left to stir for 1 hour then treated slowly with 25g (0.151 moles) of potassium iodide in 25ml of water. The mixture was left to stir until nitrogen gas evolution finished. It was extracted with two 30ml portions of methylene dichloride and the organic layer was washed with aqueous potassium bisulphite solution until the layer was decolorized. After washing with distilled water, the organic layer was dried over anhydrous magnesium sulphate, filtered and the methylene dichloride was pumped off using the rotary evaporator. The oily residue was vacuum distilled to give 22.3g (60.4%) of colourless oil identified as 1-iodo-4-(2-propyl)benzene.

Boiling point = 53-55°C at 0.5mmHg.

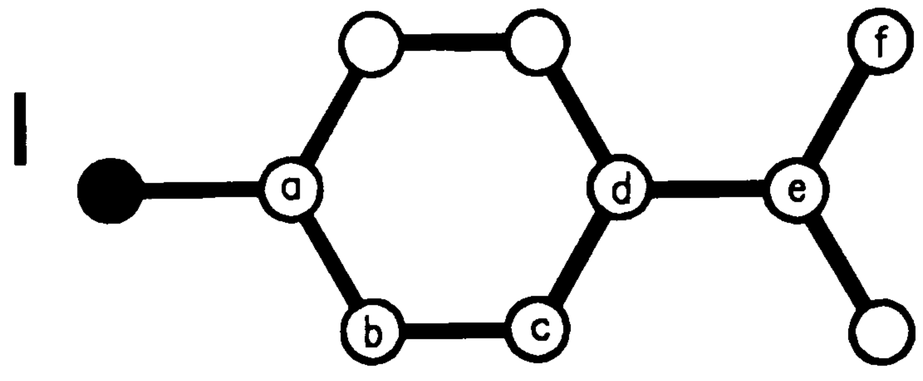
Analysis Found: C,43.7; H,4.6. $C_9H_{11}I$ requires C,43.9; H,4.5.

Infrared (KBr disc; cm^{-1}) 3097(w), 3065(w), 3051(w), 3034(w), 3016(w), 2956(s), 2921(m), 2883(m), 2862(m), 2580(w), 1898(w), 1780(w), 1641(w), 1588(w), 1487(s), 1480(m), 1460(m), 1451(w), 1442(w), 1402(s), 1383(w), 1365(w), 1331(w), 1297(w), 1268(w), 1228(w), 1182(w), 1142(w), 1118(w), 1098(m), 1064(m), 1048(w), 1007(s), 996(w), 957(w), 940(w), 920(w), 890(w), 817(s), 798(w), 781(w), 749(m), 742(w), 713(m), 588(w), 530(m).

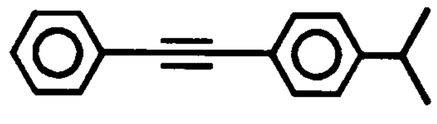
Mass spectrum (E.I.) A highest mass peak was observed at m/e 246 corresponding to the species $^{12}C_9{}^{1}H_{11}{}^{127}I$.

^{1}H N.M.R. 250.134 MHz; solvent CCl_4, referenced externally to $(CH_3)_4Si$ at 0.00ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.48 7.45 6.65 6.62	4	doublet of doublets	aromatic C(b,c)-H
2.77 2.74 2.71 2.68 2.65	1	quintet	propyl C(e)-H
1.15 1.12	6	doublet	propyl C(f)-H



4-(2-propyl)diphenylacetylene



18.75g (0.075 moles) 1-iodo-4-(2-propyl)benzene was dissolved in 20ml anhydrous pyridine and added to a mechanically stirred suspension of 12.34g (0.075 moles) phenylethynyl copper in 100ml of anhydrous pyridine under nitrogen. The mixture was refluxed for 18 hours, then cooled and poured into 300ml of distilled water. Using two 30ml portions of toluene, the organic products were extracted and then washed with two-molar hydrochloric acid, 10% aqueous sodium bicarbonate and water. The organic layer was dried with anhydrous magnesium sulphate, filtered and evaporated to give a solid residue by rotary evaporator. The residue was recrystallized from methanol to give 10.2g (61.8%) of 4-(2-propyl)diphenylacetylene.

Melting point = 84-85°C

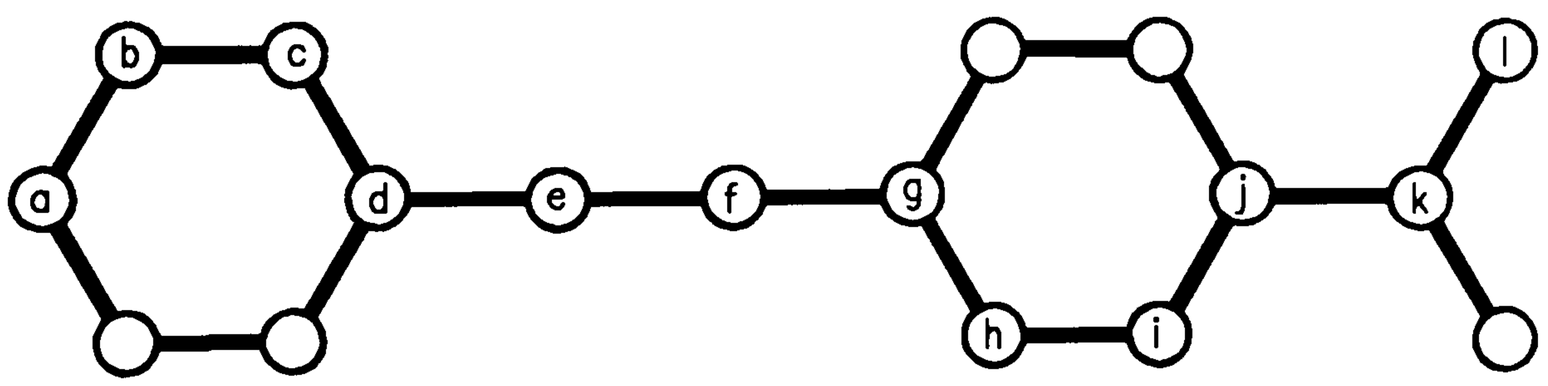
Analysis Found: C,91.9; H,7.1. $C_{17}H_{16}$ requires C,92.7; H,7.3.

Infrared (KBr disc; cm^{-1}) 3084(w), 3060(w), 3038(w), 3028(w), 2965(s), 2933(m), 2902(w), 2876(m), 2224(w), 1970(w), 1953(w), 1918(w), 1887(w), 1672(w), 1602(m), 1598(w), 1577(w), 1519(m), 1509(m), 1492(m), 1463(m), 1449(s), 1442(w), 1418(m), 1411(w), 1390(w), 1370(w), 1283(w), 1182(w), 1118(w), 1100(m), 1075(m), 1057(w), 1030(w), 1021(w), 1010(w), 919(m), 911(w), 892(w), 836(s), 822(w), 798(w), 759(s), 738(w), 700(w), 694(s), 671(w), 562(m), 531(m), 482(w), 457(w).

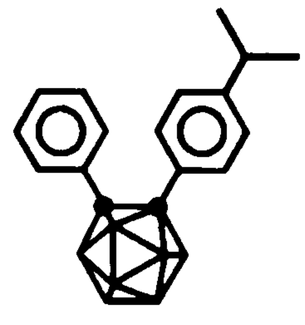
Mass spectrum (E.I.) A highest mass peak was observed at m/e 220 corresponding to the species $^{12}C_{17}{}^{1}H_{16}$.

^{1}H N.M.R. 250.134 MHz; solvent CCl_4, referenced externally to $(CH_3)_4Si$ at 0.00ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.45 7.42 6.94 6.91	4	doublet of doublets	aromatic C(h,i)-H
7.31-7.07	5	multiplet	aromatic C(a,b,c)-H
2.81 2.78 2.75 2.72 2.69	1	quintet	propyl C(k)-H
1.21 1.18	6	doublet	propyl C(l)-H



1-phenyl-2-[4-(2-propyl)phenyl]-1,2-dicarba-*closo*-dodecaborane

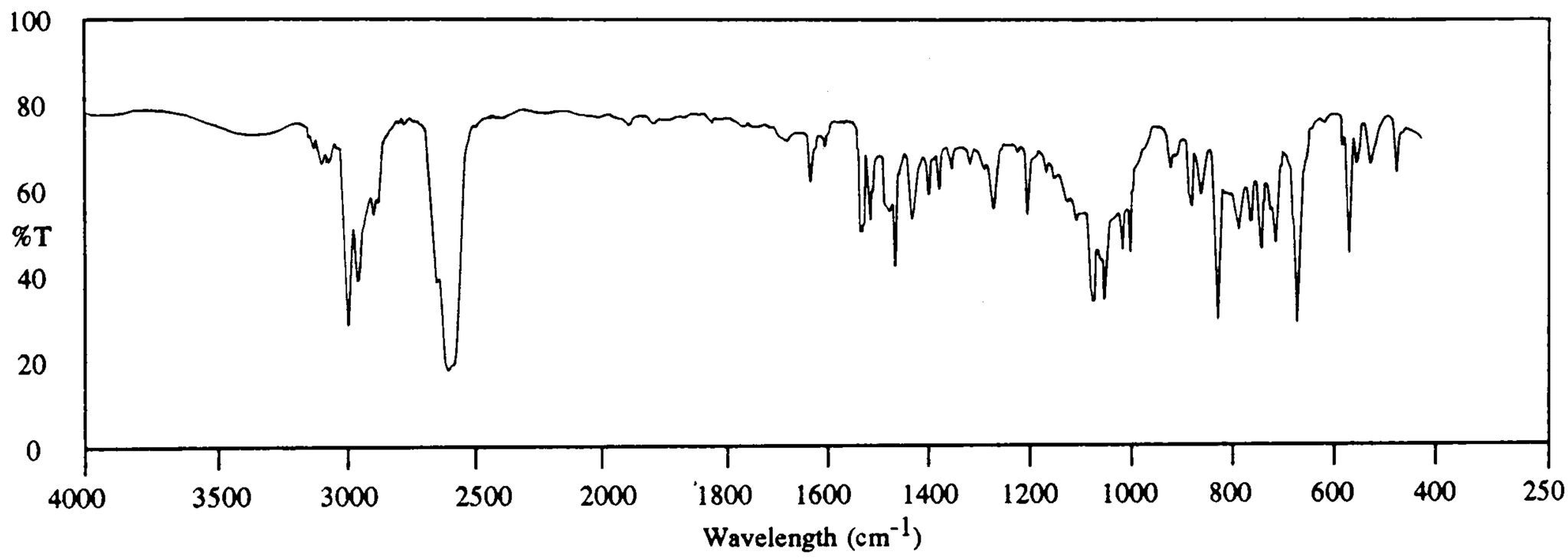


A solution of 8.8g (0.04 moles) of 4-(2-propyl)diphenylacetylene dissolved in 60ml dry toluene was added to a slurry of 8.08g (0.04 moles) of 6,9-bis(acetonitrile)-decaborane in 60ml of anhydrous toluene under a nitrogen atmosphere. The mixture was refluxed for 24 hours with gas evolution producing a dark red solution which was cooled and mixed with 50ml of methanol. After 24 hours stirring the solvents were removed by rotary evaporator and *in vacuo* to leave a solid. The residue was ground to a powder and extracted with hexane and the undissolved solid was subjected to soxhlet extraction with hexane for 24 hours. The extracts were combined and the hexane was pumped off to leave an off-white solid which was recrystallized from methanol to give 4.7g (34.8%) of 1-phenyl-2-[4-(2-propyl)phenyl]-*ortho*-carborane.

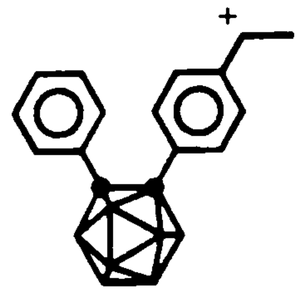
Melting point = 105-106°C

Analysis Found: C,59.9; H,7.8. $C_{17}H_{26}B_{10}$ requires C,60.4; H,7.7.

Infrared (KBr disc; cm^{-1}) 3118(w), 3100(w), 3064(w), 3041(w), 3007(w), 2965(s), 2932(m), 2922(m), 2899(w), 2876(m), 2858(w), 2639(m), 2597(s), 2581(s), 2577(s), 1611(w), 1603(w), 1585(w), 1520(w), 1517(m), 1510(w), 1498(w), 1494(w), 1470(w), 1461(w), 1451(m), 1445(w), 1419(m), 1389(w), 1369(w), 1343(w), 1310(w), 1281(w), 1266(m), 1219(w), 1201(m), 1165(w), 1152(w), 1129(w), 1124(w), 1111(w), 1081(s), 1079(s), 1064(m), 1057(s), 1037(w), 1022(m), 1009(m), 1002(w), 931(w), 924(w), 897(w), 890(w), 871(w), 842(s), 830(w), 821(w), 800(w), 779(w), 771(w), 759(m), 752(w), 747(w), 741(w), 730(m), 721(w), 706(w), 699(w), 691(s), 682(w), 634(w), 600(w), 589(m), 574(w), 549(w), 401(w), 345(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 340 corresponding to the species $^{12}C_{17}{}^{1}H_{26}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 334 and 340. A group of peaks was also present between m/e 319 and 325 and assigned to:



^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

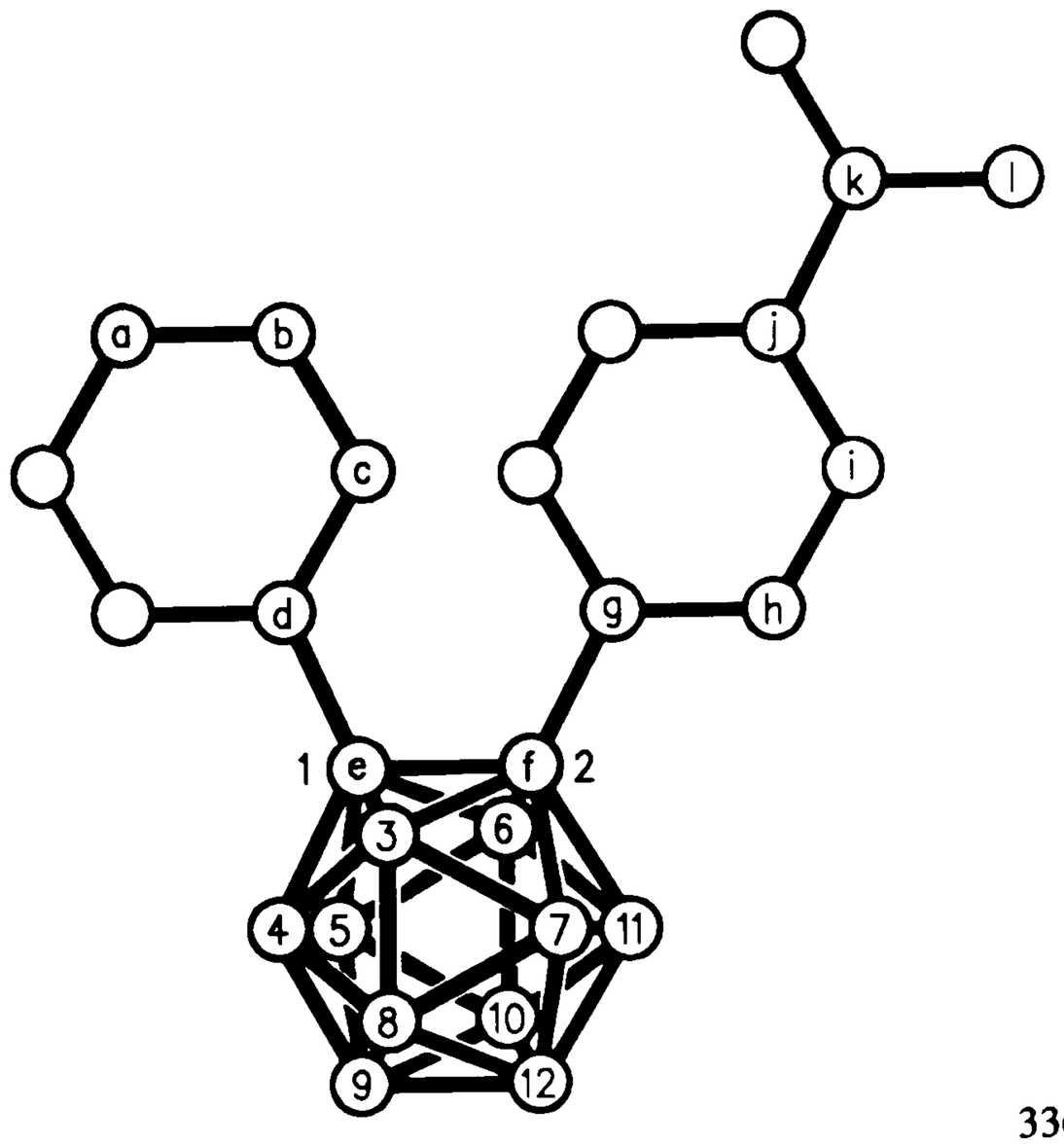
δ_{ppm}	intensity	type of peak	position of proton
7.41 7.38 6.96 6.93	4	doublet of doublets	aromatic C(h,i)-H
7.31-7.07	5	multiplet	aromatic C(a,b,c)-H
4.0-1.1	10	broad multiplet	carboranyl B-H
2.83 2.80 2.77 2.74 2.71 2.68 2.65	1	heptet	propyl C(k)-H
1.11 1.08	6	doublet	propyl C(l)-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

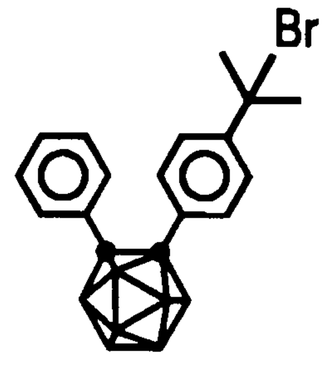
δ_{ppm}	intensity	position of boron
-4.03	2	9,12
-10.75	4	4,5,7,11
-11.91	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
151.10	j
130.52	b,c
129.94	a
128.88	d
128.09	h
126.20	i
123.53	g
85.47	f
85.17	e
33.43	k
23.45	l



1-phenyl-2-[4-(2-bromo-2-propyl)phenyl]-1,2-dicarba-*closo*-dodecaborane

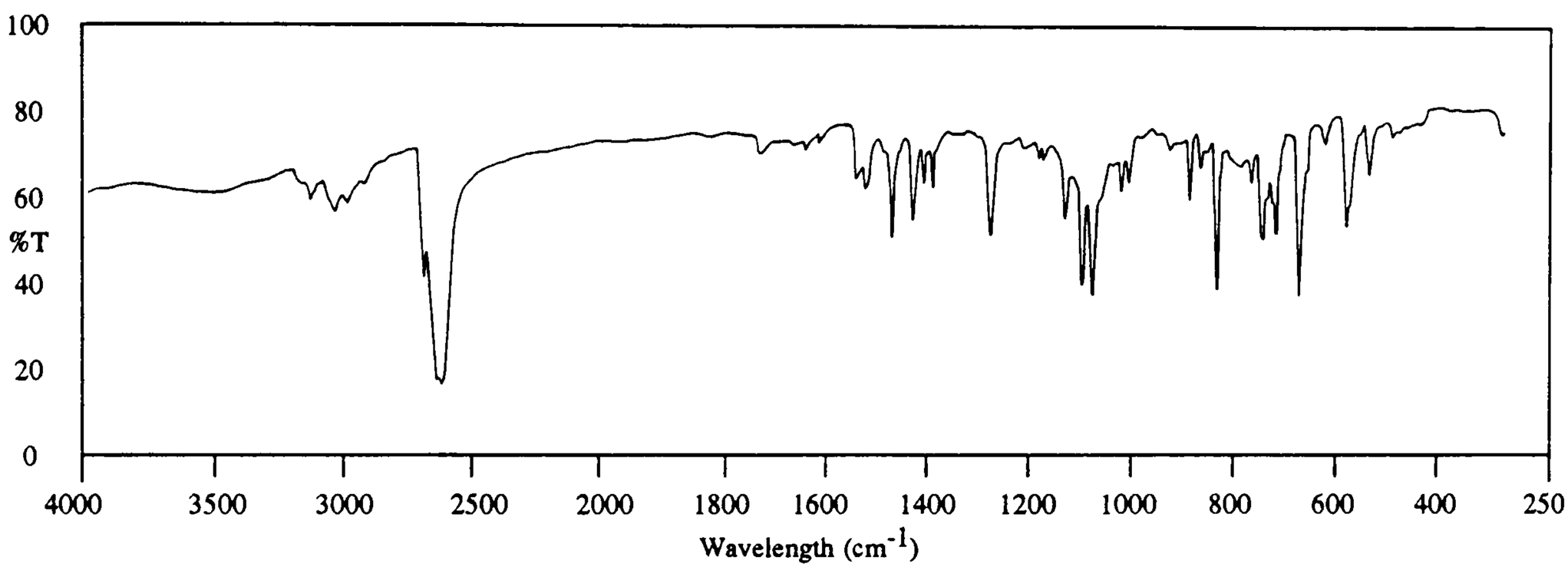


A solution of 0.68g (0.002 moles) 1-phenyl-2-[4-(2-propyl)phenyl]-*ortho*-carborane in 10ml carbon tetrachloride was added to 0.3g (0.002 moles) of N-bromosuccinimide in 10ml carbon tetrachloride with stirring. The solution was irradiated with a tungsten filament lamp, which raised the temperature to 60°C, for 4 hours. The resulting white precipitate was filtered off and the filtrate was vacuum evaporated to leave a residue which was recrystallized from hexane to produce 0.6g (72.4%) of pure 1-phenyl-2-[4-(2-bromo-2-propyl)phenyl]-*ortho*-carborane.

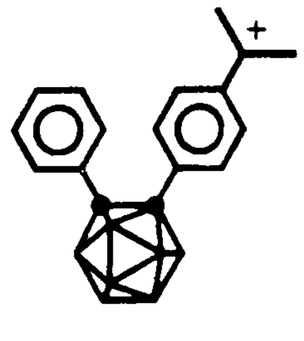
Melting point = 120-121°C

Analysis Found: C,49.5; H,6.1. $C_{17}H_{25}B_{10}Br$ requires C,48.8; H,6.0.

Infrared (KBr disc; cm^{-1}) 3100(w), 3061(w), 3044(w), 3027(w), 2996(w), 2974(w), 2952(w), 2859(w), 2641(m), 2593(s), 2581(s), 2576(s), 2570(s), 1518(w), 1511(w), 1499(w), 1495(w), 1451(m), 1412(m), 1391(w), 1374(w), 1267(m), 1176(w), 1167(w), 1128(m), 1097(s), 1090(m), 1067(s), 1060(w), 1023(w), 1009(w), 932(w), 895(w), 874(w), 861(w), 842(s), 800(w), 779(w), 758(m), 749(w), 738(w), 732(m), 727(w), 688(s), 673(w), 628(w), 599(m), 554(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 419 corresponding to the species $^{12}C_{17}{}^{1}H_{25}{}^{11}B_{10}{}^{80}Br$, accompanied by the usual carborane isotope distribution pattern between m/e 413 and 419. Peaks present between 333 and 339 were identified as:



^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

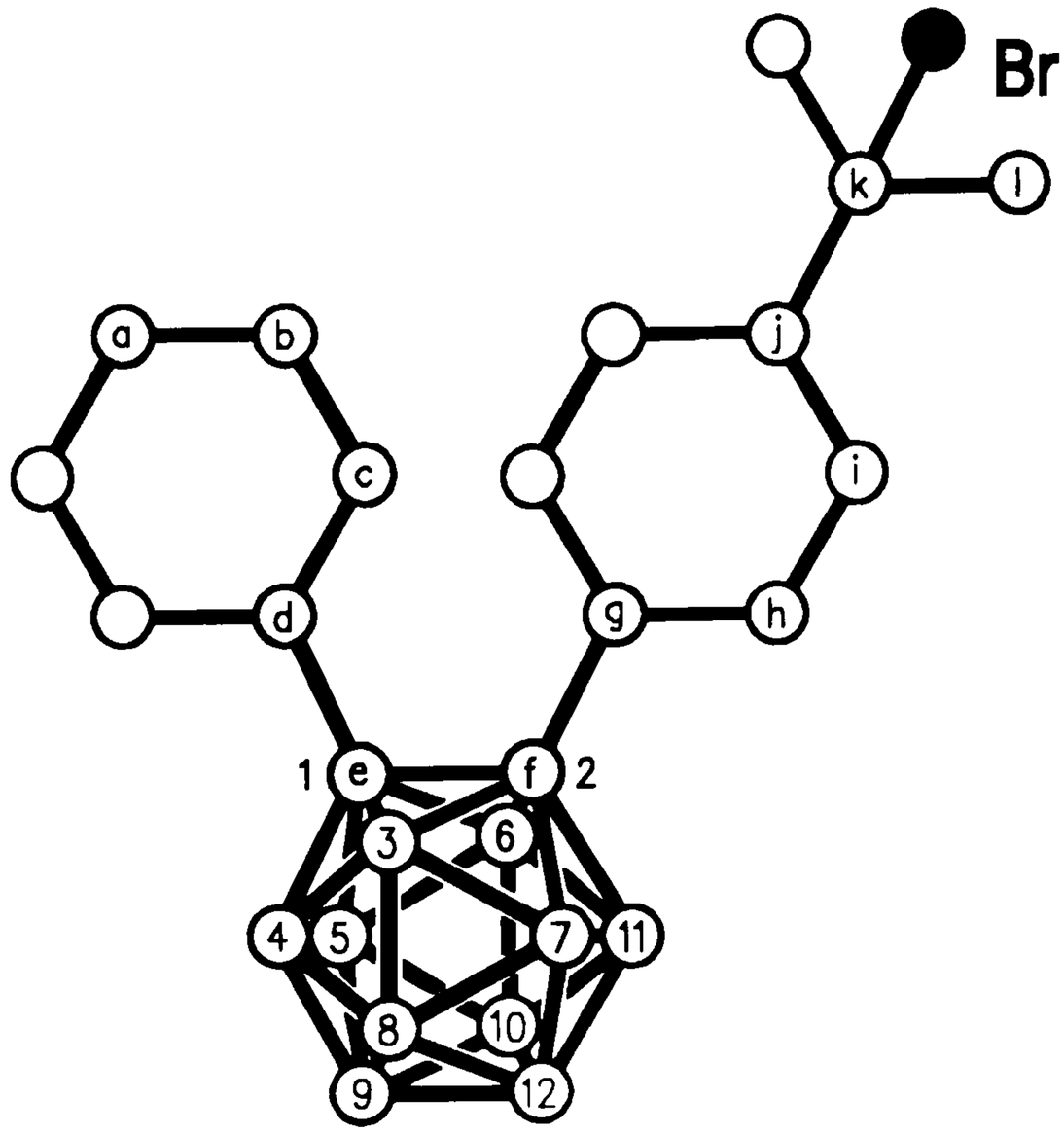
δ_{ppm}	intensity	type of peak	position of proton
7.35 7.32 7.08 7.05	4	doublet of doublets	aromatic C(h,i)-H
7.25-7.12	5	multiplet	aromatic C(a,b,c)-H
4.0-1.1	10	broad multiplet	carboranyl B-H
1.97	6	singlet	methyl C(l)-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

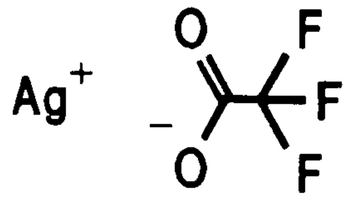
δ_{ppm}	intensity	position of boron
-2.35	2	9,12
-9.14	4	4,5,7,11
-10.15	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
135.08	j
130.52	b,c
130.17	a
129.50	d
128.26	h
125.60	i
125.15	g
114.05	k
85.28	e
84.85	f
35.08	l



Silver trifluoroacetate



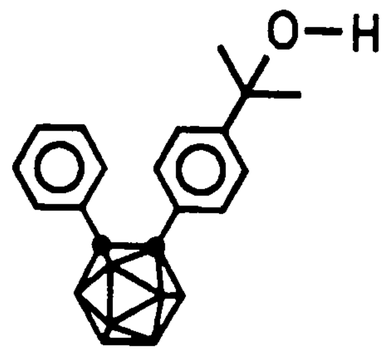
8.55g (0.075 moles) of trifluoroacetic acid was added to a suspension of 9.27g (0.04 moles) silver oxide in 40ml water. The resulting solution was filtered and the filtrate was evaporated to dryness under reduced pressure to obtain 14.6g (88.1%) of dry silver trifluoroacetate.

Analysis Found: C,10.8. $C_2AgF_3O_2$ requires C,10.9.

Attempted formation of 1-phenyl-2-(4-hydroxyphenyl)-1,2-dicarba-*closo*-dodecaborane from 1-phenyl-2-[4-(2-bromo-2-propyl)phenyl]-1,2-dicarba-*closo*-dodecaborane.

A stirred solution of 0.42g (0.001 moles) of 1-phenyl-2-[4-(2-bromo-2-propyl)phenyl]-*ortho*-carborane and 0.2ml of 30% hydrogen peroxide in 10ml diethyl ether was treated dropwise with 0.22g (0.001 moles) silver trifluoroacetate in 5ml diethyl ether at 0°C. The resulting white precipitate was filtered off and the filtrate was washed with aqueous sodium hydrogen carbonate solution, dried with anhydrous magnesium sulphate and filtered. The solvents in the organic solution were vacuum evaporated to leave a gum-like solid. The residue was extracted with hexane and 0.02g (4.4%) of insoluble 1-phenyl-2-[4-(2-trifluoroacetoxy-2-propyl)phenyl]-*ortho*-carborane was filtered off. The hexane solution gave 0.11g (31.1%) crystals of 1-phenyl-2-[4-(2-hydroxy-2-propyl)phenyl]-*ortho*-carborane.

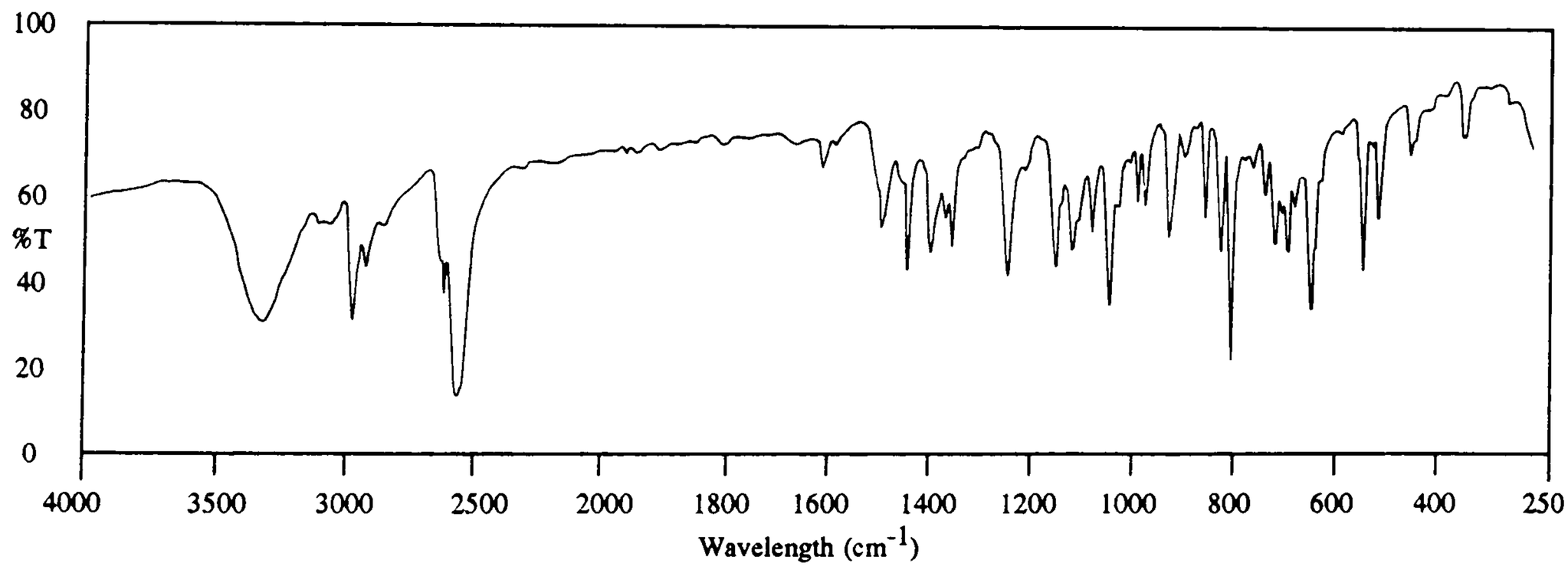
1-phenyl-2-[4-(2-hydroxy-2-propyl)phenyl]-1,2-dicarba-*closo*-dodecaborane



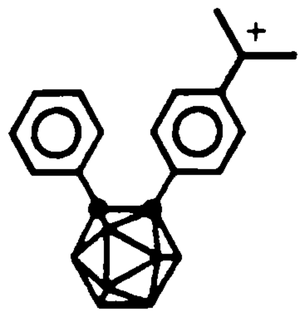
Melting point = 157-158°C

Analysis Found: C,57.2; H,7.4. $C_{17}H_{26}B_{10}O$ requires C,57.6; H,7.3.

Infrared (KBr disc; cm^{-1}) 3650-3100(s,br), 3109(w), 3096(w), 3075(w), 3062(w), 3053(w), 3032(w), 2978(s), 2938(m), 2874(w), 2860(w), 2642(m), 2637(m), 2585(s), 2579(s), 1608(w), 1584(w), 1503(w), 1498(w), 1449(m), 1407(m), 1392(w), 1378(w), 1365(m), 1344(w), 1332(w), 1320(w), 1262(m), 1230(w), 1202(w), 1172(m), 1165(w), 1141(m), 1132(w), 1104(w), 1072(s), 1058(w), 1034(w), 1019(w), 1006(w), 988(w), 974(w), 959(m), 928(w), 921(w), 907(w), 890(w), 860(m), 842(s), 831(w), 814(w), 798(w), 776(w), 757(m), 743(w), 732(m), 718(w), 689(s), 680(m), 668(w), 629(w), 597(w), 588(m), 570(w), 559(w), 498(w), 491(w), 431(w), 397(w), 391(w), 380(w), 312(w).



Mass spectrum (C.I.+) A highest mass peak was observed at m/e 356 corresponding to the species $^{12}C_{17}{}^{1}H_{26}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 350 and 356. A group of peaks at m/e 333-339 were observed and assigned to:



^{1}H N.M.R. 250.134 MHz; solvent C_6D_6 referenced to 7.15ppm.

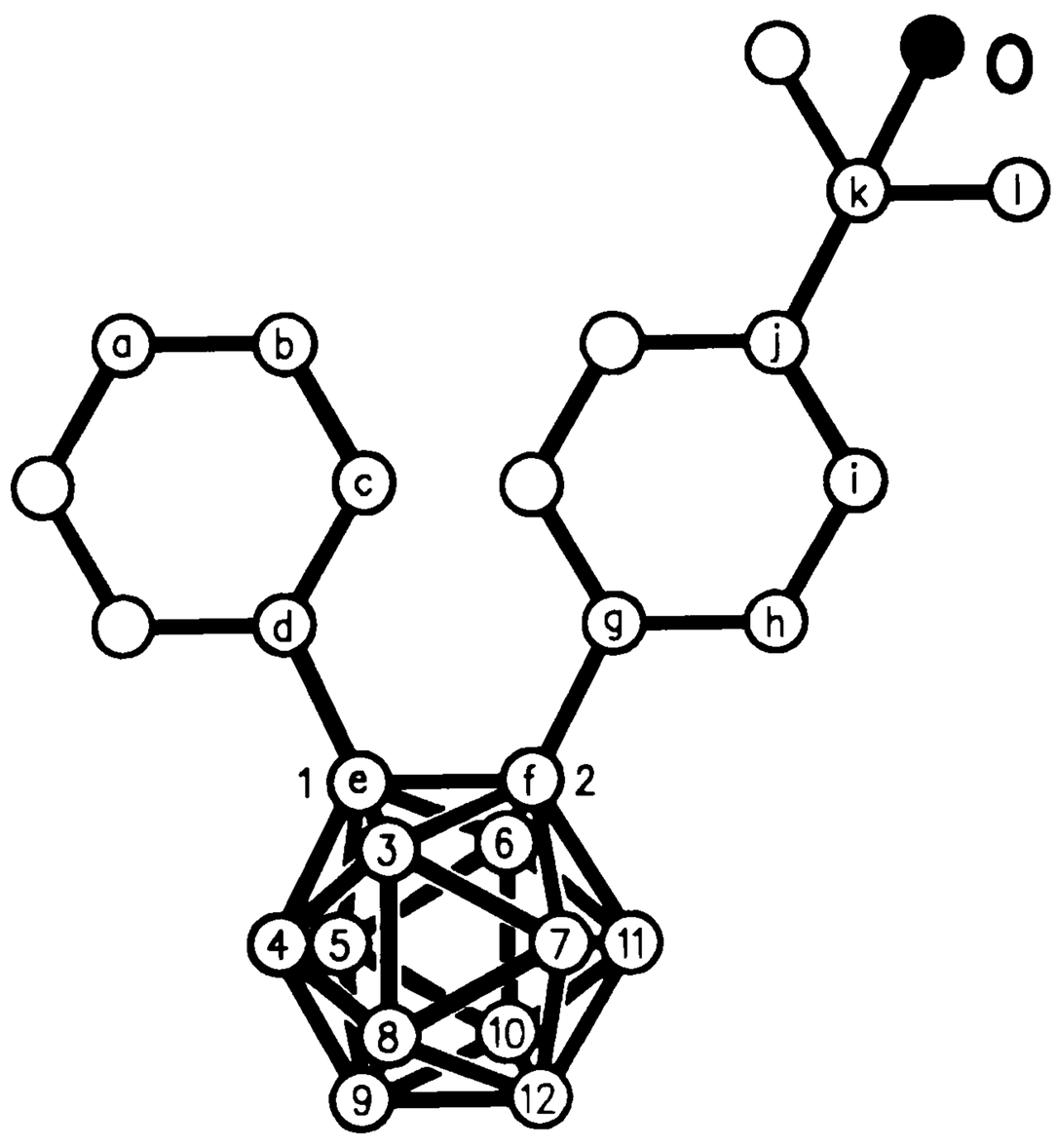
δ_{ppm}	intensity	type of peak	position of proton
8.30 8.27 7.96 7.93	4	doublet of doublets	aromatic C(h,i)-H
8.22-8.00	5	multiplet	aromatic C(a,b,c)-H
4.85	1	broad singlet	O-H
2.09	6	singlet	methyl C(l)-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

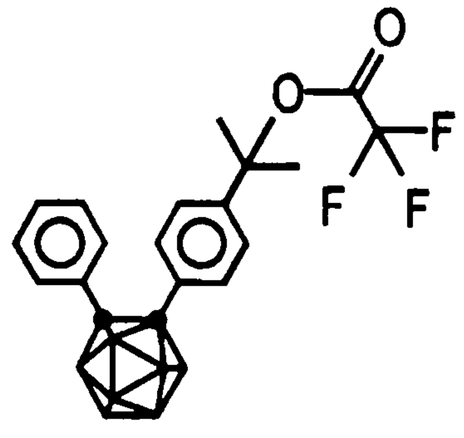
δ_{ppm}	intensity	position of boron
-2.35	2	9,12
-9.23	4	4,5,7,11
-10.23	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

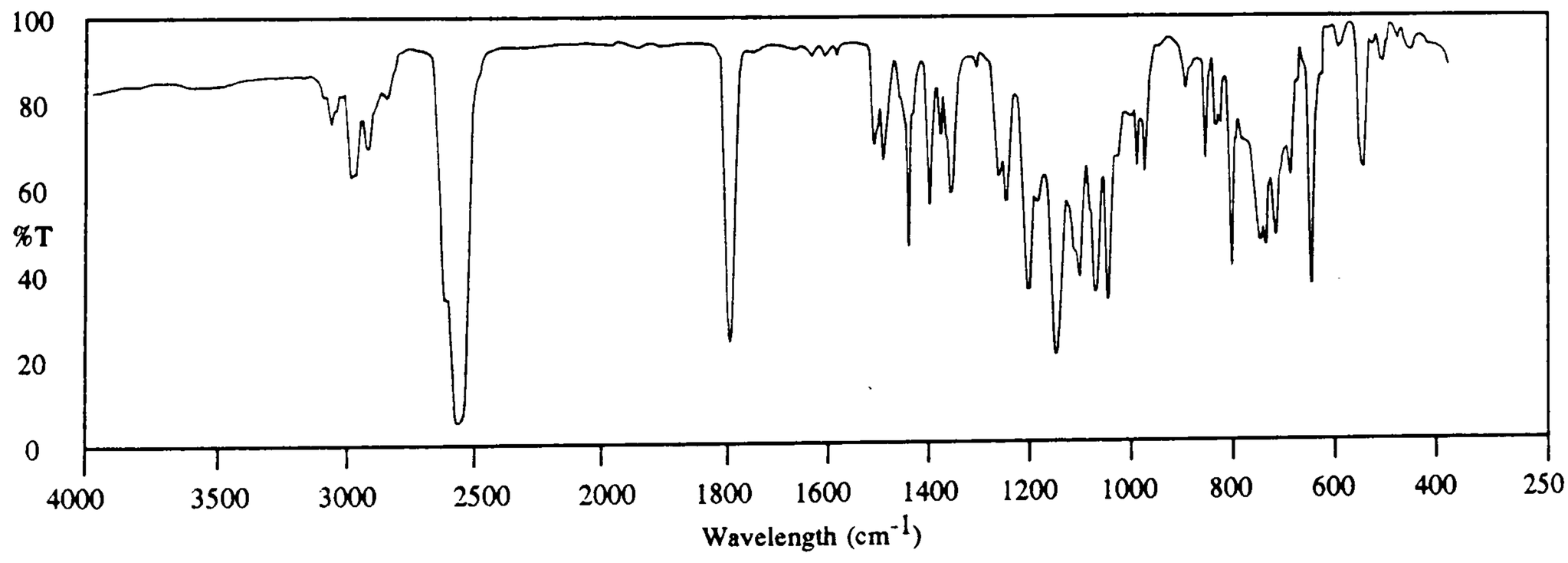
δ_{ppm}	position of carbon
151.11	j
130.06	a
129.01	d
128.18	h
125.24	g
124.29	i
85.11	e
85.04	f
72.12	k
31.52	l



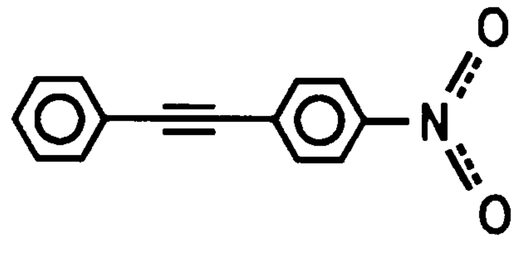
1-phenyl-2-[4-(2-trifluoroacetoxy-2-propyl)phenyl]-1,2-dicarba-*closo*-dodecaborane



Infrared (neat; cm^{-1}) 3080(w), 3062(w), 3043(w), 3026(w), 2988(w), 2975(w), 2923(w), 2908(w), 2878(w), 2857(w), 2634(s), 2587(s), 2578(s), 2572(s), 1788(s), 1632(w), 1610(w), 1584(w), 1516(w), 1510(w), 1499(w), 1468(w), 1451(m), 1445(w), 1410(m), 1391(w), 1372(w), 1321(w), 1279(w), 1267(m), 1223(s), 1208(m), 1173(s), 1136(m), 1130(m), 1100(s), 1098(s), 1076(s), 1059(w), 1034(w), 1021(w), 1007(w), 978(w), 930(w), 921(w), 892(w), 873(w), 866(w), 842(m), 820(w), 816(w), 788(m), 778(m), 773(w), 758(m), 751(w), 729(w), 724(w), 717(w), 690(s), 671(w), 639(w), 623(w), 597(w), 594(w), 589(w), 573(w), 555(w), 548(w), 535(w), 508(w), 502(w).



4-nitrodiphenylacetylene



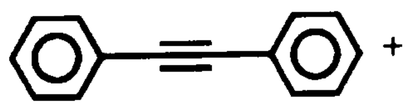
7.47g (0.03 moles) of 4-nitro-1-iodobenzene was dissolved in 20ml pyridine and added to a stirred suspension of 4.94g (0.03 moles) phenylethynyl copper in 50ml of dry pyridine under nitrogen. The mixture was heated to 120°C with stirring for 18 hours, poured into 300ml of water and extracted with ether. The ether extracts were combined, washed three times each with dilute hydrochloric acid, 10% aqueous sodium hydrogen carbonate, water, dried over magnesium sulphate and filtered. The ether was vacuum removed to leave a residue which was recrystallized from 40-60°C petroleum ether to give 4.68g (70.0%) of 4-nitrodiphenylacetylene.

Melting point = 117-118°C (lit[53]. = 120°C)

Analysis Found: C,74.3; H,3.9. $C_{14}H_9NO_2$ requires C,75.3; H,4.0.

Infrared (KBr disc; cm^{-1}) 3100(w), 3082(w), 2217(m), 1592(s), 1570(m), 1562(w), 1510(s), 1494(s), 1469(m), 1440(m), 1402(w), 1389(w), 1377(w), 1345(s), 1339(s), 1310(s), 1288(m), 1258(w), 1195(w), 1178(w), 1159(w), 1137(w), 1107(m), 1072(w), 1052(w), 1027(w), 1010(w), 997(w), 922(w), 861(s), 838(m), 768(s), 750(m), 738(w), 720(w), 691(s).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 223 corresponding to the species $^{12}C_{14}{}^{1}H_9{}^{14}N{}^{16}O_2$. A peak at m/e 177 was shown and identified as:



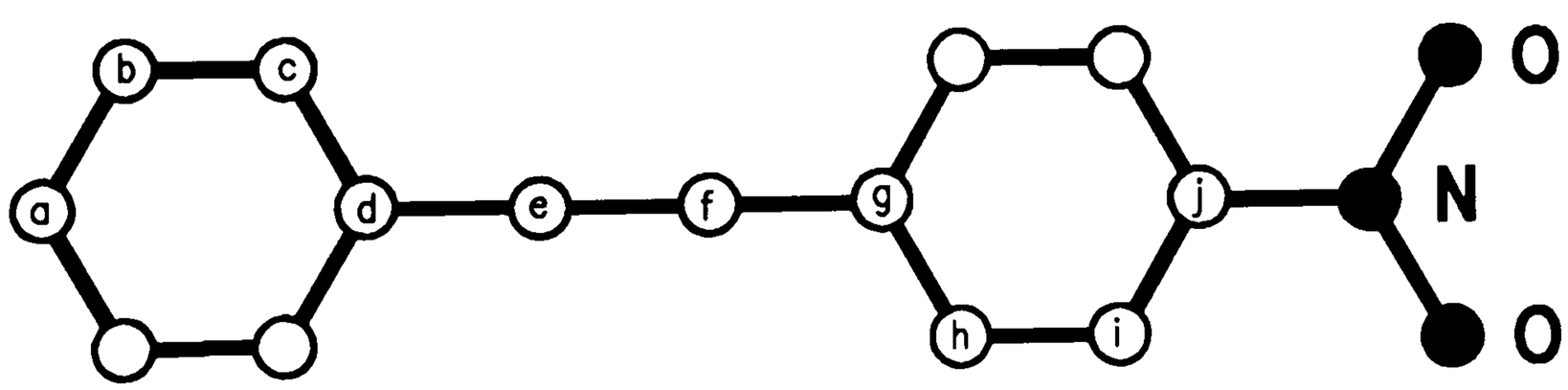
51. Stephens R.D. Castro C.E. *J. Org. Chem.* 1963 **28** 3313-3315

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

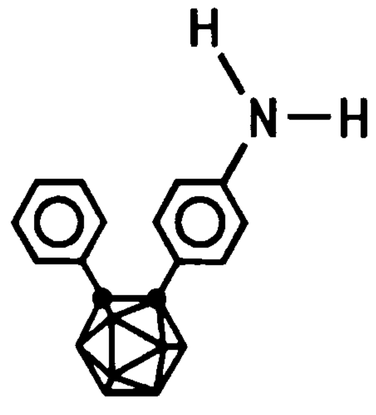
δ_{ppm}	intensity	type of peak	position of proton
8.24 8.21 7.68 7.65	4	doublet of doublets	aromatic C(h,i)-H
7.95-7.91 7.60-7.52	5	multiplet	aromatic C(a,b,c)-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
145.16	j
132.26	c
131.85	b
129.26	a
128.53	h
127.99	g
124.79	d
122.10	i
90.03	f
87.53	e



1-phenyl-2-(4-aminophenyl)-1,2-dicarba-*closo*-dodecaborane

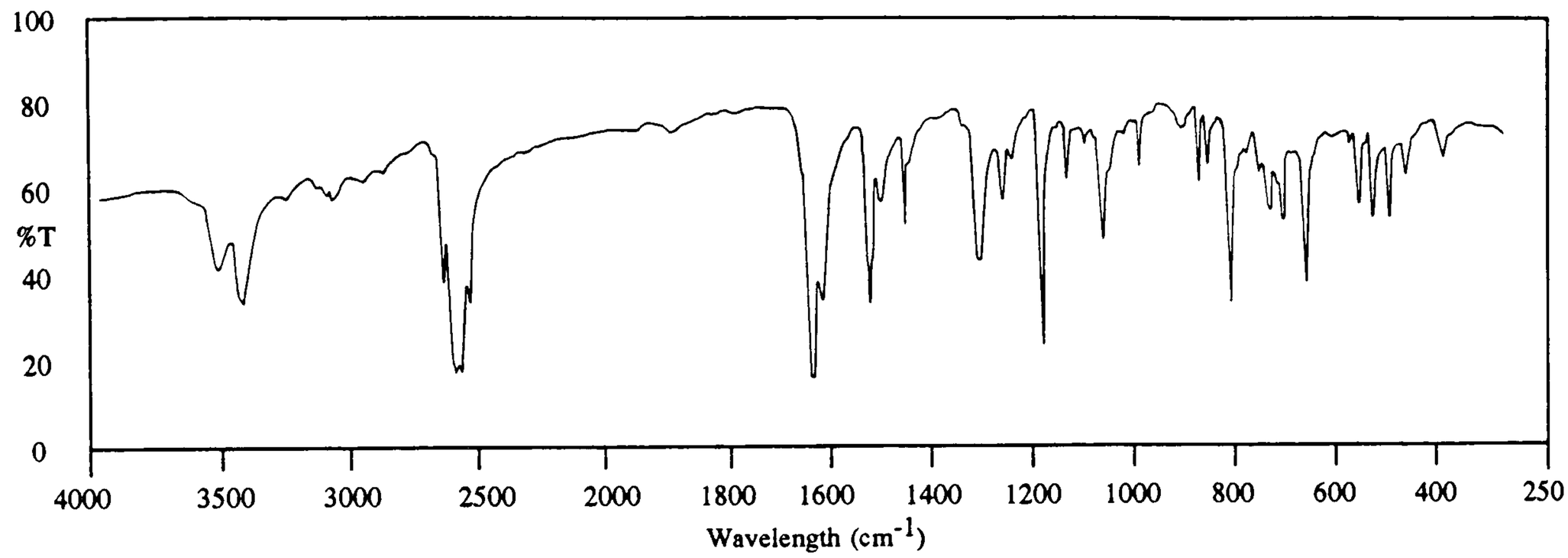


4.46g (0.02 moles) of 4-nitrodiphenylacetylene dissolved in 40ml dry toluene was added to a suspension of 4.04g (0.02 moles) 6,9-bis(acetonitrile)-decaborane in 40ml dry toluene under nitrogen. On heating the solution to refluxing temperature, gas evolution appeared and quickly ceased. The green solution was refluxed for 24 hours, cooled, diluted with 30ml methanol and stirred for 12 hours. The solvents were pumped off leaving a solid which was subjected to soxhlet extraction for 24 hours with hexane. The extract was concentrated by removing some hexane using rotary evaporator and 0.51g (8.2%) crystals were obtained and identified as 1-phenyl-2-(4-aminophenyl)-*ortho*-carborane.

Melting point =166-167°C

Analysis Found: C,53.9; H,6.6; N,3.9. $C_9H_{18}B_{10}$ requires C,54.0; H,6.8; N,4.5.

Infrared (KBr disc; cm^{-1}) 3465(m), 3379(m), 3208(m), 3081(w), 3058(w), 3037(w), 2627(m), 2588(s), 2564(s), 2532(m), 1622(s), 1604(m), 1514(m), 1510(w), 1493(w), 1490(w), 1448(m), 1441(w), 1338(w), 1309(m), 1262(w), 1243(w), 1189(s), 1072(m), 1060(w), 1032(w), 1003(w), 925(w), 917(w), 889(m), 872(w), 831(s), 817(w), 797(w), 773(w), 752(m), 738(w), 729(m), 687(s), 599(w), 581(m), 567(w), 555(m), 523(m), 490(w), 418(w).



Ultraviolet (solvent MeOH, nm) 267(broad), 297(shoulder).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 313 corresponding to the species $^{12}C_{14}{}^{1}H_{21}{}^{11}B_{10}{}^{14}N$, accompanied by the usual carborane isotope distribution pattern between m/e 307 and 313. Two peaks at m/e 92 and 77 were also seen identified respectively as:

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

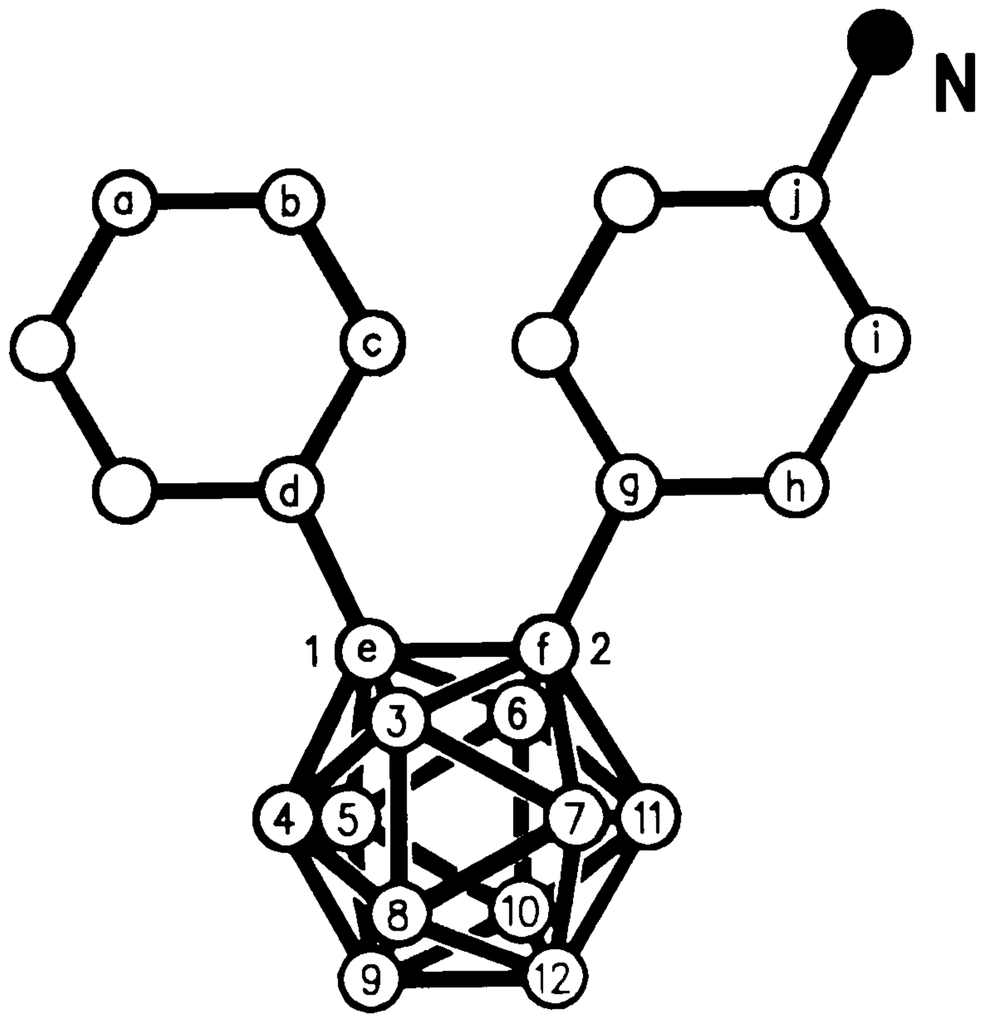
δ_{ppm}	intensity	type of peak	position of proton
7.37 7.34 6.31 6.28	4	doublet of doublets	aromatic C(h,i)-H
7.18-7.04	5	multiplet	aromatic C(a,b,c)-H
3.59	2	broad singlet	N-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-3.07	2	9,12
-9.58	4	4,5,7,11
-11.09	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
147.64	j
131.89	h
130.64	c
129.94	a
128.13	b
120.62	g
114.16	i
86.76	f
85.54	e



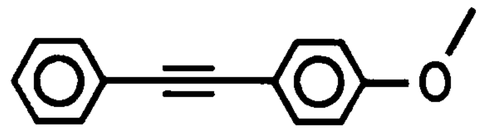
Attempted formation of 1-phenyl-2-(4-hydroxyphenyl)-1,2-dicarba-*closo*-dodecaborane from 1-phenyl-2-(4-aminophenyl)-1,2-dicarba-*closo*-dodecaborane.

0.08g (0.001 moles) sodium nitrite in 2ml concentrated sulphuric acid was added to a solution of 0.31g (0.001 moles) 1-phenyl-2-(4-aminophenyl)-*ortho*-carborane in 5ml glacial acetic acid. The mixture was stirred for 1 hour when the solution went red and 10ml of water was added. The mixture was heated to 80°C for an hour with no sign of any gas being produced. When the mixture cooled, diethyl ether was added which gave rapid gas evolution. The organic layer was separated, washed with water, dried over anhydrous magnesium sulphate, filtered and finally pumped to dryness to give 0.17g (57.4%) of 1,2-diphenyl-*ortho*-carborane.

Melting point = 143-145°C (lit[54]. = 148-149°C)

52. Stanko V.I. Kopylov V.V. Klimova A.I. *J. Gen. Chem. U.S.S.R.* 1965 **35** 1437-1439

4-methoxydiphenylacetylene



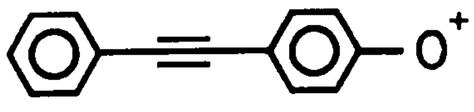
Under nitrogen, a solution of 17.6g (0.075 moles) of 4-iodoanisole dissolved in 20ml dry pyridine was added to a slurry of 12.3g (0.075 moles) of phenylethynyl copper in 100ml dry pyridine and refluxed for 18 hours with stirring. After cooling, the mixture was poured into 300ml of water and the aqueous solution was extracted four times with diethyl ether. The ether extracts were combined and washed three times each with dilute hydrochloric acid, aqueous sodium hydrogen carbonate solution and water. Ether was pumped off by rotary evaporator to leave a dark residue which was dissolved in hot methanol and decolorized with activated charcoal. After filtering off the charcoal, 10.4g (66.7%) of 4-methoxydiphenylacetylene was obtained.

Melting point = 58-59°C (lit[53]. = 60°C)

Analysis Found: C,86.4; H,5.8. $C_{15}H_{12}O$ requires C,86.5; H,5.8.

Infrared (KBr disc; cm^{-1}) 3091(w), 3053(w), 3031(w), 3008(w), 2998(w), 2955(w), 2938(w), 2900(w), 2839(w), 2532(w),2214(m), 2022(w), 1952(w), 1904(w), 1882(w), 1830(w), 1751(w), 1668(w), 1656(w), 1603(s), 1591(s), 1564(m), 1560(m), 1542(w), 1506(s), 1496(m), 1458(m), 1439(s), 1412(w), 1382(w), 1365(w), 1328(w), 1313(w), 1300(w), 1287(s), 1248(s), 1172(s), 1157(w), 1138(m), 1107(m), 1068(m), 1026(s), 1002(w), 992(w), 978(w), 947(w), 915(w), 839(s), 820(m), 817(w), 779(m), 754(s), 721(w), 690(s), 669(w), 653(w), 640(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 208 corresponding to the species $^{12}C_{15}{}^{1}H_{12}{}^{16}O$. A peak at m/e 193 shown was identified as:

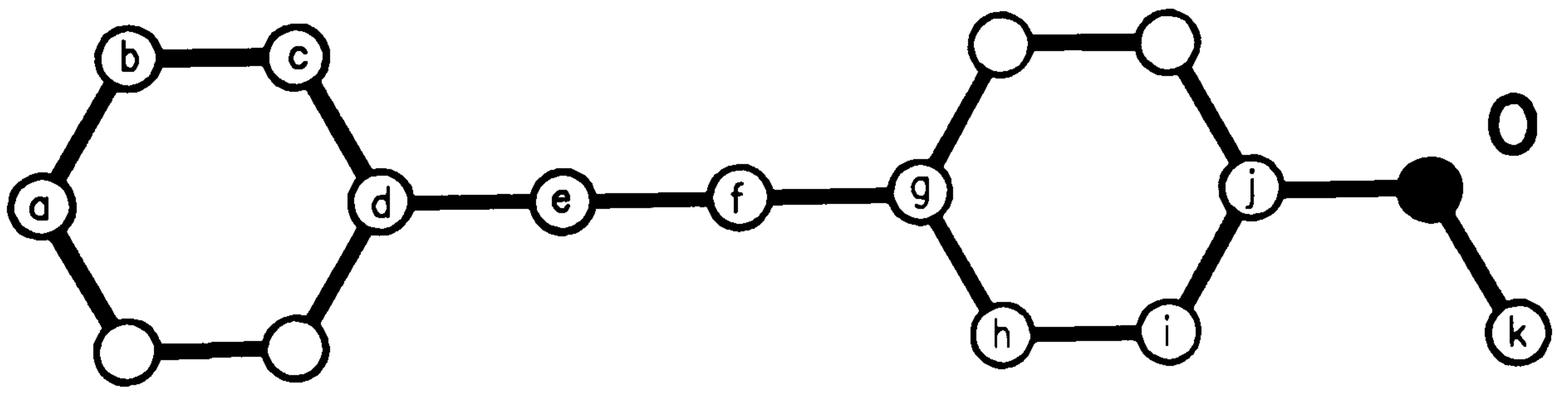


^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

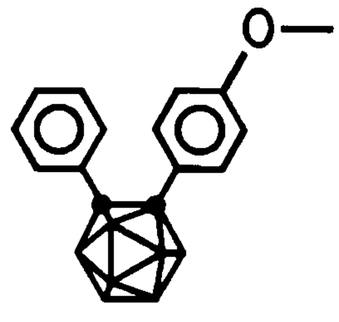
δ_{ppm}	intensity	type of peak	position of proton
7.52 7.49 6.91 6.88	4	doublet of doublets	aromatic C(h,i)-H
7.57-7.34	5	multiplet	aromatic C(a,b,c)-H
3.83	3	singlet	methyl C-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
159.55	j
133.23	b
131.17	h
128.47	c
128.01	a
123.53	d
115.29	g
114.16	i
89.36	e
88.04	f
55.22	k



1-phenyl-2-(4-methoxyphenyl)-1,2-dicarba-*closo*-dodecaborane

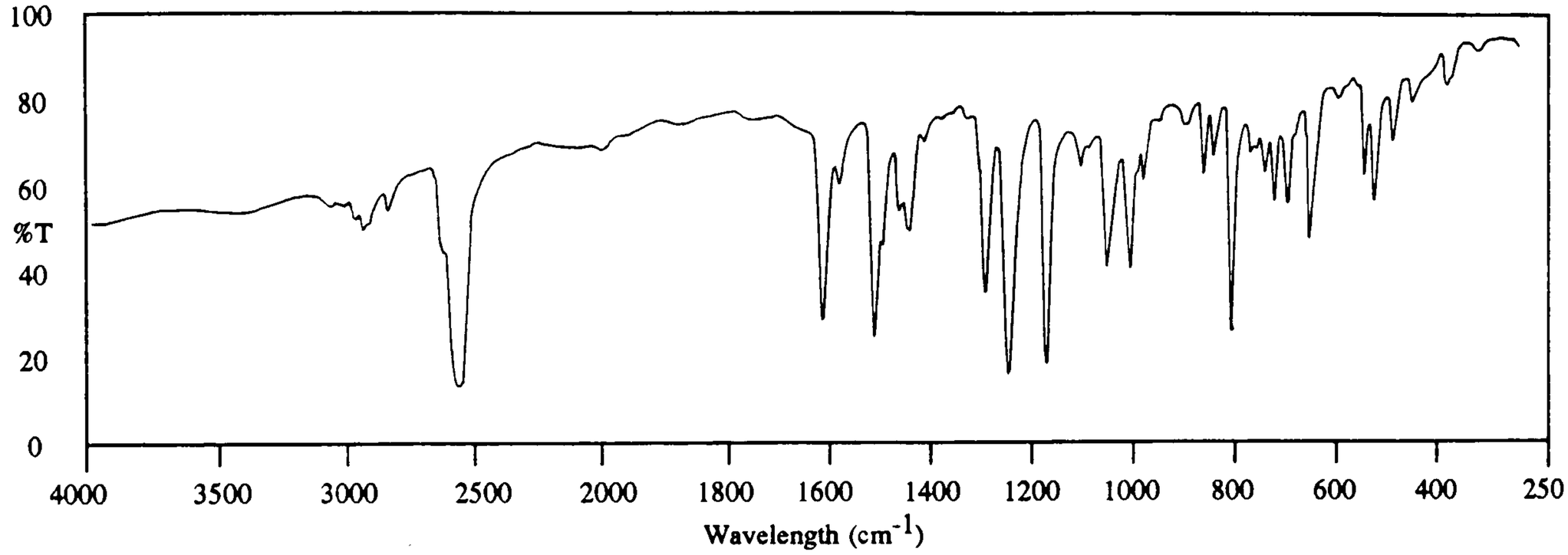


A solution of 10.3g (0.05 moles) of 4-methoxydiphenylacetylene in 40ml dry toluene was added to a suspension of 10.1g (0.05 moles) 6,9-bis(acetonitrile)-decaborane in 60ml dry toluene under nitrogen. The mixture was refluxed for 24 hours with hydrogen evolution giving a dark red solution. At 20°C the solution was diluted with 60ml methanol and stirred for 5 hours. The solvents were vacuum evaporated to leave a solid which was ground to a powder and subjected to soxhlet extraction with 80ml of hexane for 24 hours. The solution was concentrated by removing some hexane *in vacuo* and crystallized from hexane. 6.4g (39.6%) of 1-phenyl-2-(4-methoxyphenyl)-*ortho*-carborane was obtained.

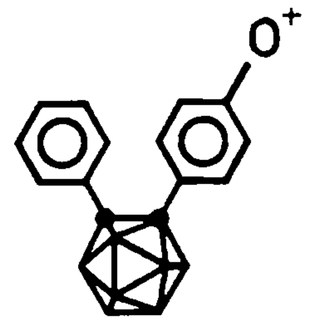
Melting point = 101-102°C

Analysis Found: C,55.4; H,6.6. $C_{15}H_{22}B_{10}O$ requires C,55.2; H,6.8.

Infrared (KBr disc; cm^{-1}) 3058(w), 3000(w), 2961(w), 2933(w), 2919(w), 2838(w), 2632(m), 2579(s), 1602(m), 1575(w), 1508(m), 1498(m), 1459(w),1441(m), 1414(w), 1381(w), 1331(w), 1298(m), 1257(s), 1182(s), 1163(w), 1131(w), 1105(w), 1072(m), 1028(m), 1013(w), 1002(w), 982(w), 940(w), 932(w), 890(w), 871(w), 838(m), 801(w), 792(w), 773(w), 756(w), 728(w), 687(m), 636(w), 581(w), 562(w), 529(w), 491(w), 425(w), 418(w), 368(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 328 corresponding to the species $^{12}C_{15}{}^{1}H_{22}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 322 and 328. Presence of peaks between m/e 307 and 313 were assigned to:



^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

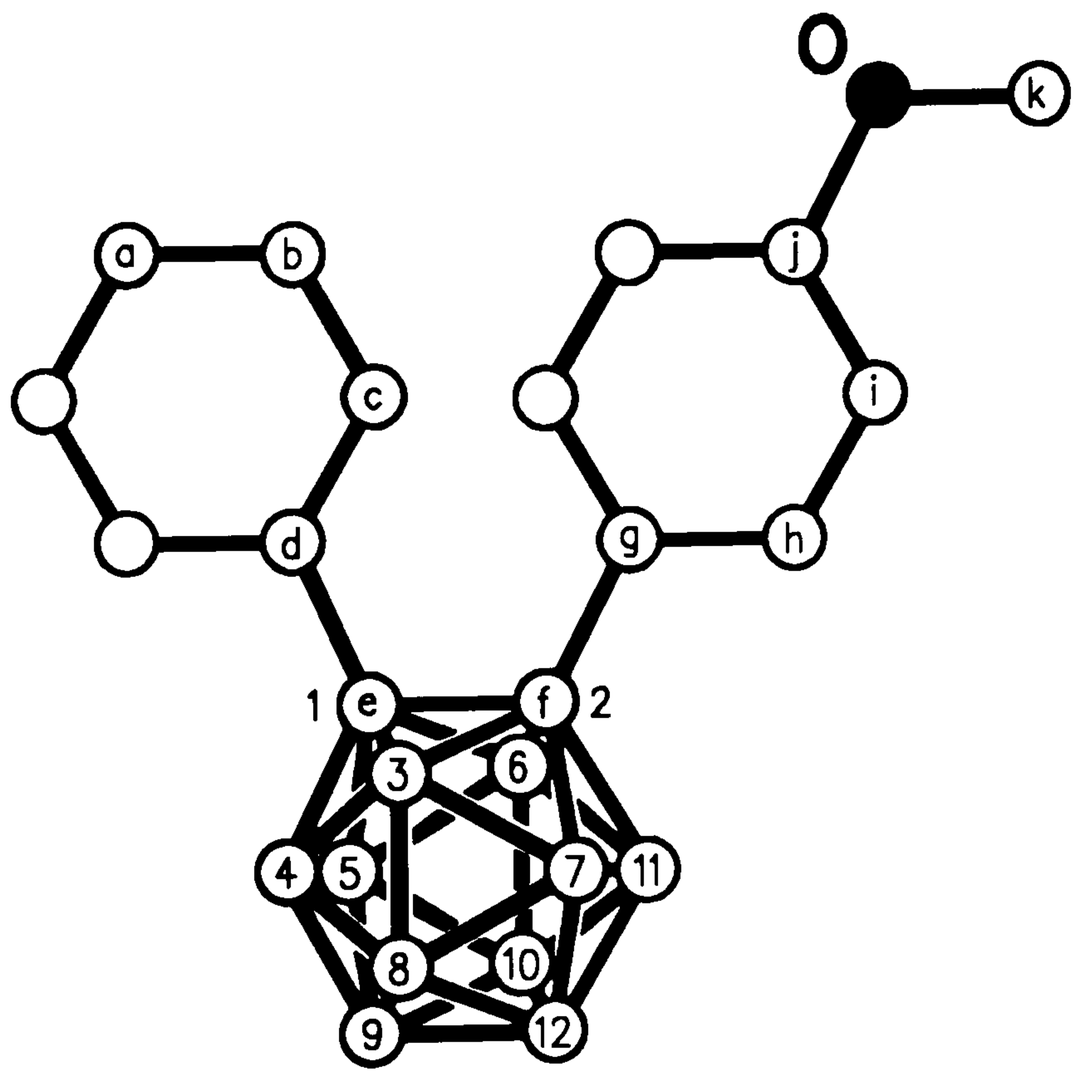
δ_{ppm}	intensity	type of peak	position of proton
7.45 7.41 6.72 6.68	4	doublet of doublets	aromatic C(h,i)-H
7.55-7.52 7.34-7.20	5	multiplet	aromatic C(a,b,c)-H
3.70	3	singlet	methyl C-H
3.8-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-2.49	2	9,12
-9.13	4	4,5,7,11
-10.50	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
160.30	j
131.54	h
130.15	c
129.57	a
127.75	b
122.47	g
112.96	i
85.19	f
84.89	e
54.74	k



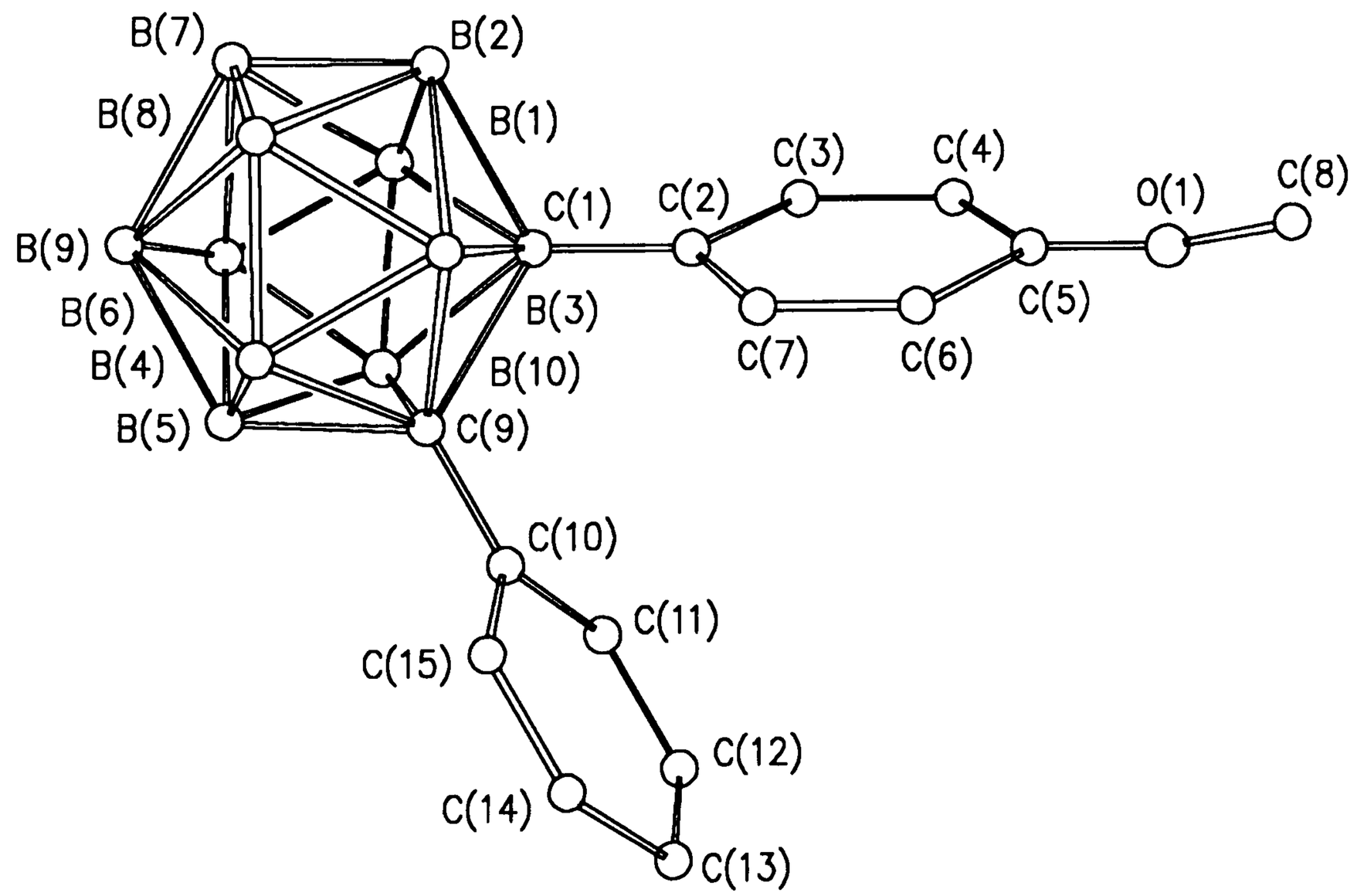
X-ray Analysis (W. Clegg, Newcastle University)

Crystallographic data, CuK_α radiation

Formula = $C_{15}H_{22}B_{10}O$
Formula weight, M_r = 326.4
System = monoclinic
Space Group = $P2_1/n$
a = 11.181(2)Å
b = 40.007(7)Å
c = 17165(3)Å
α = 90°
β = 97.58(2)°
γ = 90°
Unit cell volume, V = 7611.1Å^3
Calculated density, D_c = 1.139gcm^{-3}
Number of formulae per unit cell, Z = 16
Absorption coefficient, μ = 0.41mm^{-1}
F(000) = 2720 electrons

Number of unique reflections = 11248
Observed reflections, $F > 2\sigma_c(F)$ = 7487
$2\theta_{max}$ = 120°
Range, 2θ = 25 to 35°
Range, h = -12 to 12
Range, k = 0 to 44
Range, l = 0 to 19

Measure of overall precision of data, R_{sigma} = 0.048
Crystal size = 0.24 x 0.32 x 0.36mm
Crystal colour = colourless
Temperature, T = 295°K



Bond lengths (Å)

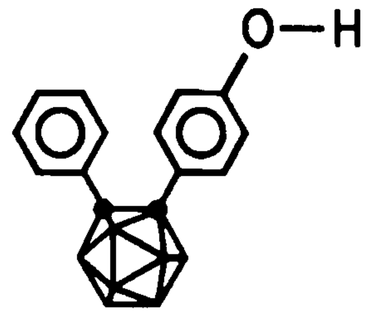
C(1)-C(2)	1.495(5)		C(1)-C(9)	1.737(5)
C(1)-B(10)	1.715(5)		C(1)-B(1)	1.703(6)
C(1)-B(2)	1.692(6)		C(1)-B(3)	1.727(5)
C(2)-C(3)	1.374(5)		C(2)-C(7)	1.377(5)
C(3)-C(4)	1.372(6)		C(4)-C(5)	1.369(5)
C(5)-C(6)	1.369(6)		C(5)-O(1)	1.361(5)
C(6)-C(7)	1.379(6)		C(8)-O(1)	1.411(8)
C(9)-C(10)	1.505(5)		C(9)-B(10)	1.716(5)
C(9)-B(3)	1.718(5)		C(9)-B(4)	1.706(5)
C(9)-B(5)	1.705(6)		C(10)-C(11)	1.379(6)
C(10)-C(15)	1.375(6)		C(11)-C(12)	1.381(6)
C(12)-C(13)	1.364(9)		C(13)-C(14)	1.355(9)
C(14)-C(15)	1.377(7)		B(10)-B(1)	1.770(6)
B(10)-B(5)	1.769(6)		B(10)-B(6)	1.763(6)
B(1)-B(2)	1.752(6)		B(1)-B(6)	1.757(7)
B(1)-B(7)	1.761(6)		B(2)-B(3)	1.766(6)
B(2)-B(7)	1.763(7)		B(2)-B(8)	1.778(6)
B(3)-B(4)	1.770(6)		B(3)-B(8)	1.755(6)
B(4)-B(5)	1.768(6)		B(4)-B(8)	1.756(7)
B(4)-B(9)	1.765(6)		B(5)-B(6)	1.768(6)
B(5)-B(9)	1.761(7)		B(6)-B(7)	1.761(7)
B(6)-B(9)	1.769(6)		B(7)-B(8)	1.744(6)
B(7)-B(9)	1.770(7)		B(8)-B(9)	1.768(7)

Bond angles (°)

C(2)-C(1)-C(9)	118.4(3)		C(2)-C(1)-B(10)	117.5(3)
C(9)-C(1)-B(10)	59.6(2)		C(2)-C(1)-B(1)	122.2(3)
C(9)-C(1)-B(1)	109.3(3)		B(10)-C(1)-B(1)	62.4(2)
C(2)-C(1)-B(2)	123.1(3)		C(9)-C(1)-B(2)	109.2(2)
B(10)-C(1)-B(2)	112.5(3)		B(1)-C(1)-B(2)	62.1(2)
C(2)-C(1)-B(3)	119.0(3)		C(9)-C(1)-B(3)	59.5(2)
B(10)-C(1)-B(3)	110.3(3)		B(1)-C(1)-B(3)	112.4(3)
B(2)-C(1)-B(3)	62.2(2)		C(1)-C(2)-C(3)	121.5(3)
C(1)-C(2)-C(7)	121.0(3)		C(3)-C(2)-C(7)	117.4(3)
C(2)-C(3)-C(4)	121.6(3)		C(3)-C(4)-C(5)	120.4(4)
C(4)-C(5)-C(6)	119.1(4)		C(4)-C(5)-O(1)	123.5(4)
C(6)-C(5)-O(1)	117.4(3)		C(5)-C(6)-C(7)	120.1(3)
C(2)-C(7)-C(6)	121.4(3)		C(1)-C(9)-C(10)	119.1(3)
C(1)-C(9)-B(10)	59.6(2)		C(10)-C(9)-B(10)	118.9(3)
C(1)-C(9)-B(3)	60.0(2)		C(10)-C(9)-B(3)	117.9(3)
B(10)-C(9)-B(3)	110.7(3)		C(1)-C(9)-B(4)	109.7(3)
C(10)-C(9)-B(4)	121.3(3)		B(10)-C(9)-B(4)	112.8(3)
B(3)-C(9)-B(4)	62.2(2)		C(1)-C(9)-B(5)	109.4(3)
C(10)-C(9)-B(5)	122.1(3)		B(10)-C(9)-B(5)	62.3(2)
B(3)-C(9)-B(5)	112.7(3)		B(4)-C(9)-B(5)	62.4(2)
C(9)-C(10)-C(11)	121.4(3)		C(9)-C(10)-C(15)	120.4(3)
C(11)-C(10)-C(15)	118.1(4)		C(10)-C(11)-C(12)	120.2(4)
C(11)-C(12)-C(13)	120.9(5)		C(12)-C(13)-C(14)	119.1(5)
C(13)-C(14)-C(15)	120.8(5)		C(10)-C(15)-C(14)	120.9(4)
C(5)-O(1)-C(8)	118.6(3)		C(1)-B(10)-C(9)	60.8(2)
C(1)-B(10)-B(1)	58.5(2)		C(9)-B(10)-B(1)	107.2(3)
C(1)-B(10)-B(5)	107.5(3)		C(9)-B(10)-B(5)	58.6(2)
B(1)-B(10)-B(5)	108.2(3)		C(1)-B(10)-B(6)	105.6(3)
C(9)-B(10)-B(6)	105.8(3)		B(1)-B(10)-B(6)	59.7(3)
B(5)-B(10)-B(6)	60.1(2)		C(1)-B(1)-B(10)	59.1(2)
C(1)-B(1)-B(2)	58.6(2)		B(10)-B(1)-B(2)	107.1(3)
C(1)-B(1)-B(6)	106.4(3)		B(10)-B(1)-B(6)	60.0(3)
B(2)-B(1)-B(6)	108.1(3)		C(1)-B(1)-B(7)	106.1(3)
B(10)-B(1)-B(7)	107.7(3)		B(2)-B(1)-B(7)	60.2(3)
B(6)-B(1)-B(7)	60.1(3)		C(1)-B(2)-B(1)	59.2(2)
C(1)-B(2)-B(3)	59.9(2)		B(1)-B(2)-B(3)	108.2(3)
C(1)-B(2)-B(7)	106.5(3)		B(1)-B(2)-B(7)	60.1(3)
B(3)-B(2)-B(7)	107.7(3)		C(1)-B(2)-B(8)	106.5(3)
B(1)-B(2)-B(8)	108.2(3)		B(3)-B(2)-B(8)	59.4(2)
B(7)-B(2)-B(8)	60.2(3)		C(1)-B(3)-C(9)	60.5(2)
C(1)-B(3)-B(2)	57.9(2)		C(9)-B(3)-B(2)	106.6(3)
C(1)-B(3)-B(4)	107.3(3)		C(9)-B(3)-B(4)	58.5(2)
B(2)-B(3)-B(4)	108.4(3)		C(1)-B(3)-B(8)	105.9(3)
C(9)-B(3)-B(8)	105.6(3)		B(2)-B(3)-B(8)	60.6(3)
B(4)-B(3)-B(8)	59.7(3)		C(9)-B(4)-B(3)	59.2(2)
C(9)-B(4)-B(5)	58.8(2)		B(3)-B(4)-B(5)	107.3(3)
C(9)-B(4)-B(8)	106.1(3)		B(3)-B(4)-B(8)	59.7(3)
B(5)-B(4)-B(8)	108.0(3)		C(9)-B(4)-B(9)	105.7(3)
B(3)-B(4)-B(9)	107.6(3)		B(5)-B(4)-B(9)	59.8(3)
B(8)-B(4)-B(9)	60.3(3)		C(9)-B(5)-B(10)	59.2(2)
C(9)-B(5)-B(4)	58.8(2)		B(10)-B(5)-B(4)	107.4(3)
C(9)-B(5)-B(6)	106.0(3)		B(10)-B(5)-B(6)	59.8(2)
B(4)-B(5)-B(6)	108.0(3)		C(9)-B(5)-B(9)	105.9(3)
B(10)-B(5)-B(9)	107.8(3)		B(4)-B(5)-B(9)	60.0(3)
B(6)-B(5)-B(9)	60.2(3)		B(10)-B(6)-B(1)	60.4(3)
B(10)-B(6)-B(5)	60.1(2)		B(1)-B(6)-B(5)	108.8(3)
B(10)-B(6)-B(7)	107.9(3)		B(1)-B(6)-B(7)	60.1(3)
B(5)-B(6)-B(7)	108.1(3)		B(10)-B(6)-B(9)	107.6(3)
B(1)-B(6)-B(9)	108.4(3)		B(5)-B(6)-B(9)	59.7(2)
B(7)-B(6)-B(9)	60.2(3)		B(1)-B(7)-B(2)	59.6(3)

B(1)-B(7)-B(6)	59.9(3)		B(2)-B(7)-B(6)	107.5(3)
B(1)-B(7)-B(8)	108.0(3)		B(2)-B(7)-B(8)	60.3(3)
B(6)-B(7)-B(8)	107.7(3)		B(1)-B(7)-B(9)	108.2(3)
B(2)-B(7)-B(9)	108.2(3)		B(6)-B(7)-B(9)	60.1(3)
B(8)-B(7)-B(9)	59.8(3)		B(2)-B(8)-B(3)	60.0(3)
B(2)-B(8)-B(4)	108.5(3)		B(3)-B(8)-B(4)	60.5(3)
B(2)-B(8)-B(7)	59.5(3)		B(3)-B(8)-B(7)	107.7(3)
B(4)-B(8)-B(7)	108.3(3)		B(2)-B(8)-B(9)	107.6(3)
B(3)-B(8)-B(9)	108.1(3)		B(4)-B(8)-B(9)	60.1(3)
B(7)-B(8)-B(9)	59.9(3)		B(4)-B(9)-B(5)	60.2(3)
B(4)-B(9)-B(6)	108.1(3)		B(5)-B(9)-B(6)	60.1(3)
B(4)-B(9)-B(7)	108.1(3)		B(5)-B(9)-B(7)	108.1(3)
B(6)-B(9)-B(7)	59.7(3)		B(4)-B(9)-B(8)	59.6(3)
B(5)-B(9)-B(8)	107.8(3)		B(6)-B(9)-B(8)	107.6(3)
B(7)-B(9)-B(8)	60.2(3)			

1-phenyl-2-(4-hydroxyphenyl)-1,2-dicarba-*closo*-dodecaborane

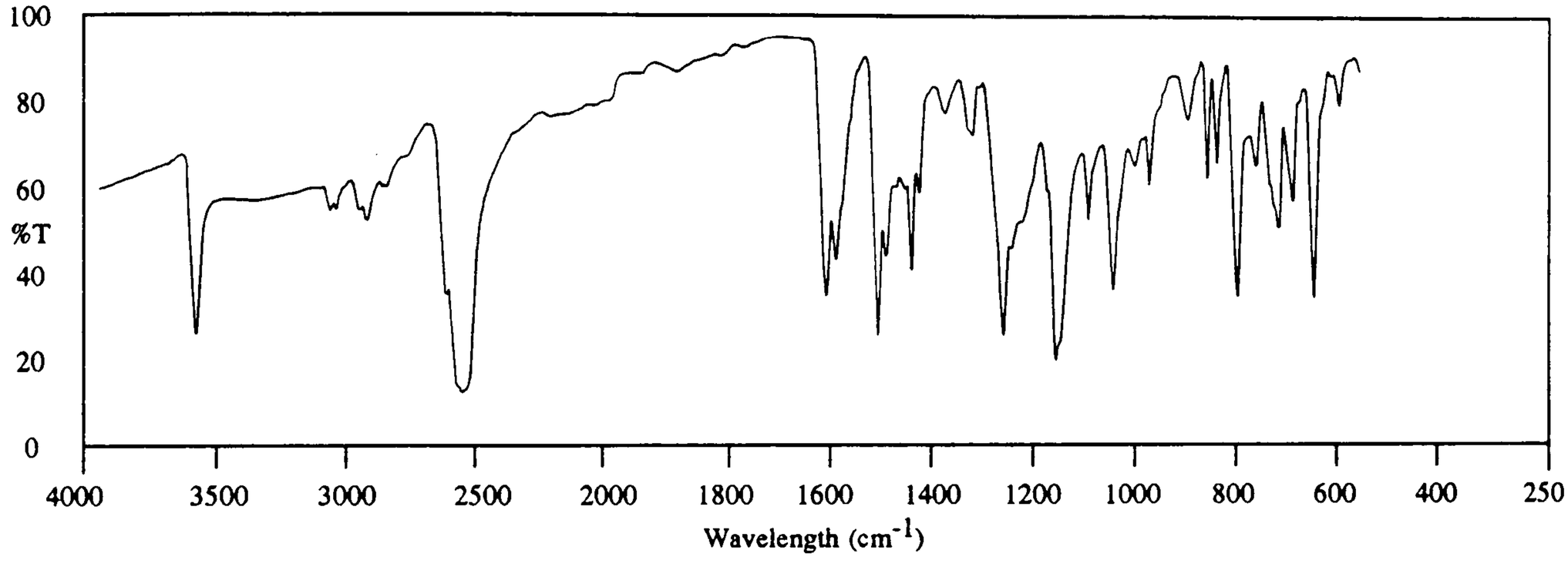


Dry hydrogen chloride was bubbled through 8ml of pyridine and the resulting solid was heated to 170°C. After two hours, 1.96g (0.006 moles) of 1-phenyl-2-(4-methoxyphenyl)-*ortho*-carborane was added while the temperature was at 170°C and then raised to 200°C for 3 hours. It was left to cool and formed a white solid of which a large part was dissolved in water to leave a gum-like solid. The undissolved solid was filtered off, dried, dissolved in diethyl ether, dried over anhydrous magnesium sulphate and filtered. The ether was vacuum-removed from the filtrate to yield a white solid. It was recrystallized from hexane to give 1.24g (66.2%) of 1-phenyl-2-(4-hydroxyphenyl)-ortho-carborane.

Melting point = 136-137°C

Analysis Found: C,54.0; H,6.6. $C_{14}H_{20}B_{10}O$ requires C,53.9; H,6.4.

Infrared (KBr disc; cm^{-1}) 3563(s), 3066(w), 3042(w), 3016(w), 2967(w), 2928(w), 2858(w), 2642(m), 2604(s), 2572(s), 2552(s), 1612(s), 1591(m), 1515(s), 1497(m), 1467(w), 1448(m), 1432(m), 1384(w), 1337(w), 1333(w), 1279(s), 1263(m), 1192(w), 1180(s), 1173(s), 1119(m), 1108(m), 1073(m), 1036(w), 1022(w), 1007(w), 984(w), 931(w), 921(w), 913(w), 894(w), 878(w), 840(m), 802(m), 788(w), 760(m), 731(m), 715(w), 693(m), 659(w), 641(w), 580(w), 554(w), 526(w), 489(w), 428(w), 368(w), 355(w).



Ultraviolet (solvent MeOH, nm) 228(sharp), 233(shoulder), 265(w), 274(w), 283(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 314 corresponding to the species $^{12}C_{14}{}^{1}H_{20}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 308 and 314.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

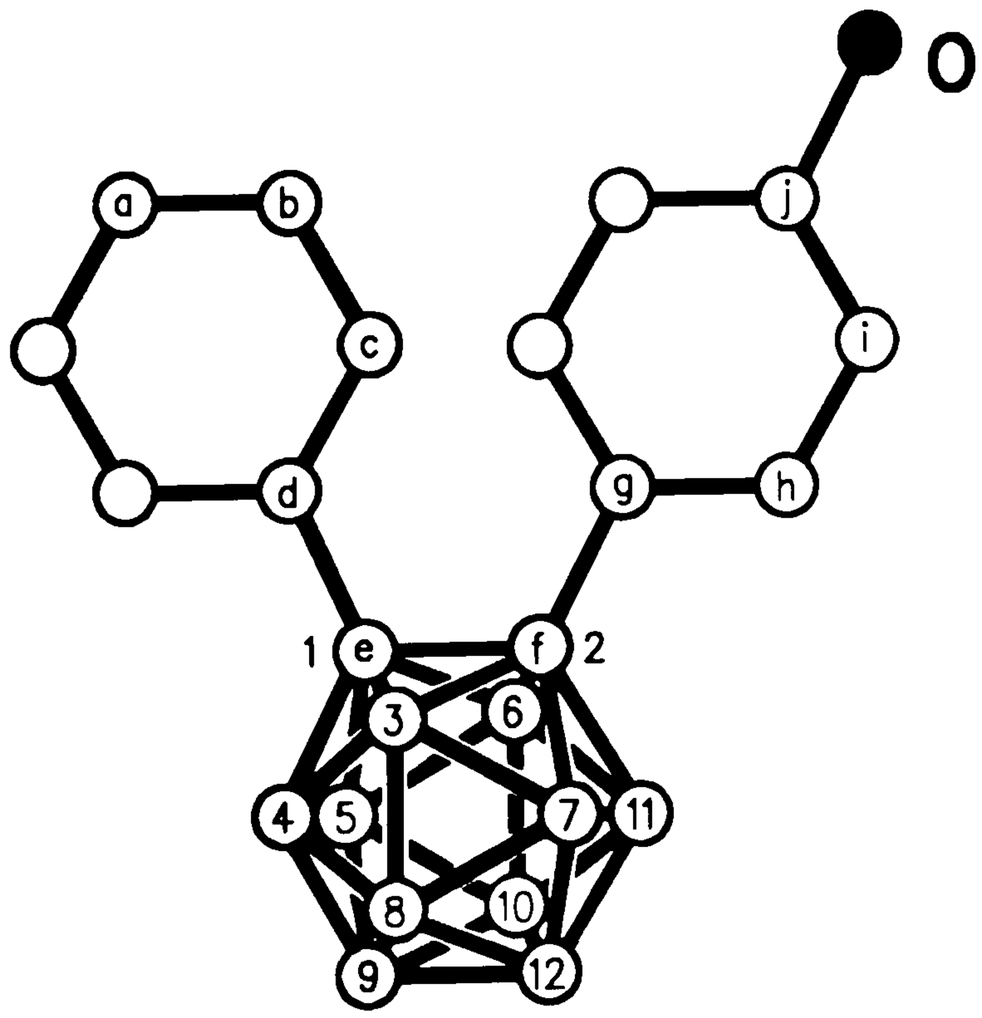
δ_{ppm}	intensity	type of peak	position of proton
7.34 7.31 6.47 6.44	4	doublet of doublets	aromatic C-H
7.21-7.02	5	multiplet	aromatic C-H
4.79	1	broad singlet	O-H
3.9-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

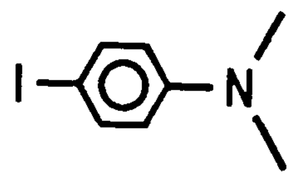
δ_{ppm}	intensity	position of boron
-2.45	2	9,12
-9.07	4	4,5,7,11
-10.44	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
156.44	j
131.84	h
130.18	c
129.63	a
127.78	b
122.50	g
114.56	i
84.95	e,f



N,N-dimethyl-4-iodoaniline



12.1g (0.1 moles) N,N-dimethylaniline was dissolved in 100ml of glacial acetic acid and 15.2g (0.06 moles) of iodine was added to the stirred solution. After 48 hours stirring, the dark purple solution was poured into 300ml of water. The precipitated black grainy matter was filtered off, washed with water, dissolved in 50ml alcohol and decolorized with aqueous sodium thiosulphate solution. The colourless organic layer was diluted with water to give a white precipitate. The precipitate was filtered off and recrystallized from absolute ethanol to give 20.2g (81.8%) of N,N-dimethyl-4-iodoaniline.

Melting point = 81-82°C (lit[55]. = 82°C)

Analysis Found: C,38.6; H,4.0; N,5.4. $C_8H_{10}IN$ requires C,38.9; H,4.1; N,5.7.

Infrared (KBr disc; cm^{-1}) 3084(w), 3075(w), 2981(w), 2928(w), 2917(w), 2892(w), 2884(w), 2852(w), 2805(w), 1869(w), 1734(w), 1604(w), 1591(s), 1557(w), 1501(s), 1448(m), 1428(w), 1408(w), 1358(s), 1316(m), 1264(w), 1232(m), 1227(m), 1197(m), 1170(m), 1129(m), 1068(m), 1028(w), 988(w), 950(w), 807(s), 750(m), 696(w).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 247 corresponding to the species $^{12}C_8{}^{1}H_{10}{}^{127}I{}^{14}N$.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
7.48 7.45 6.50 6.47	4	doublet of doublets	aromatic C-H
2.91	6	singlet	methyl C-H

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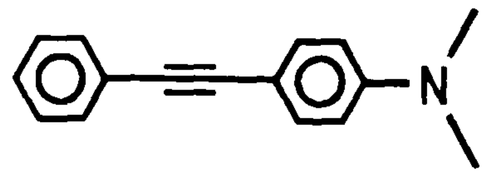
N,N-dimethylaminodiphenylacetylene



12.35g (0.05 moles) of N,N-dimethyl-4-iodoaniline was dissolved in 40ml of dry pyridine and added to a stirred suspension of 8.23g (0.05 moles) phenylethynyl copper in 120ml anhydrous pyridine under a nitrogen atmosphere. The mixture was heated to reflux for 16 hours. The dark brown solution was cooled and poured into 500ml of water. The organic layer was extracted by diethyl ether in three 30ml portions. The combined ether extracts were washed with dilute hydrochloric acid, aqueous sodium bicarbonate and then distilled water. The organic layer was dried with anhydrous magnesium sulphate, filtered and the organic solvents were driven off by rotary evaporator to leave a residue. The residue was recrystallized from methanol to give 1.15g (22.8%) of 1,4-diphenylbutadiyne and then with the mother liqour concentrated by evaporation 4.4g (40.2%) of 4-N,N-dimethylaminodiphenylacetylene was obtained.

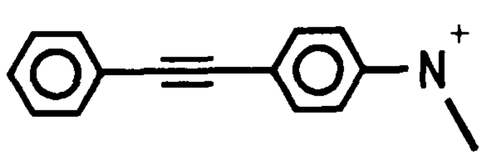
Melting point = 108-109°C

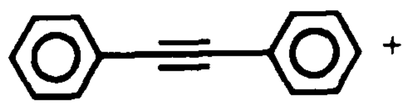
Analysis Found: C,86.9; H,7.1; N,5.8. $C_{16}H_{15}N$ requires C,86.9; H,6.8; N,6.3.

Infrared (KBr disc; cm^{-1}) 3096(w), 3074(w), 3056(w), 3041(w), 3032(w), 2994(w), 2938(w), 2920(w), 2891(w), 2864(w), 2856(w), 2807(w), 2210(m), 2159(w), 1886(w), 1612(s), 1595(s), 1571(w), 1522(s), 1487(w), 1447(m), 1362(m), 1322(w), 1276(w), 1263(w), 1229(m), 1200(m), 1200(m), 1178(w), 1160(w), 1138(m), 1127(w), 1072(w), 1063(w), 1027(w), 1008(w), 989(w), 974(w), 947(w), 921(w), 851(w), 829(w), 822(m), 758(m), 693(m).

Ultraviolet (solvent MeOH, nm) 305(shoulder), 319(shoulder), 323(sharp).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 221 corresponding to the species $^{12}C_{16}{}^{1}H_{15}{}^{14}N$. Two other peaks were seen at m/e 206 and 177 identified respectively as:



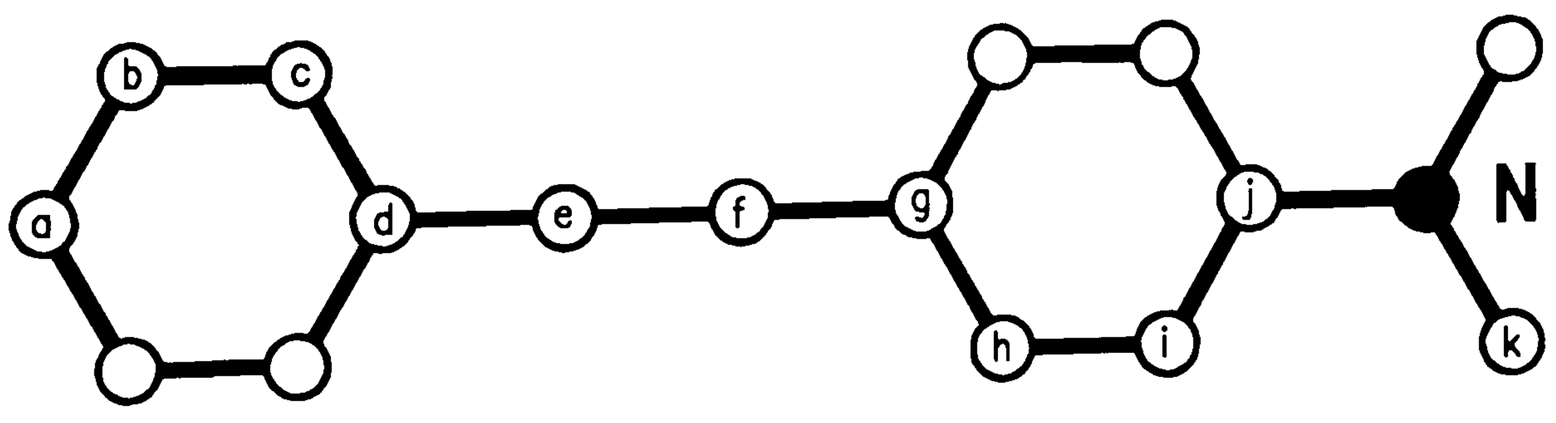


^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

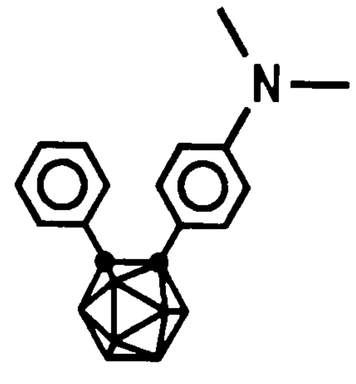
δ_{ppm}	intensity	type of peak	position of proton
7.45 7.42 6.69 6.66	4	doublet of doublets	aromatic C(h,i)-H
7.54-7.29	5	multiplet	aromatic C(a,b,c)-H
3.00	6	singlet	methyl C-H

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
150.14	j
132.68	h
131.26	c
128.19	b
127.39	a
124.20	d
111.86	i
110.14	g
90.61	f
87.32	e
40.15	k



1-phenyl-2-(4-N,N-dimethylaminophenyl)-1,2-dicarba-*closo*-dodecaborane

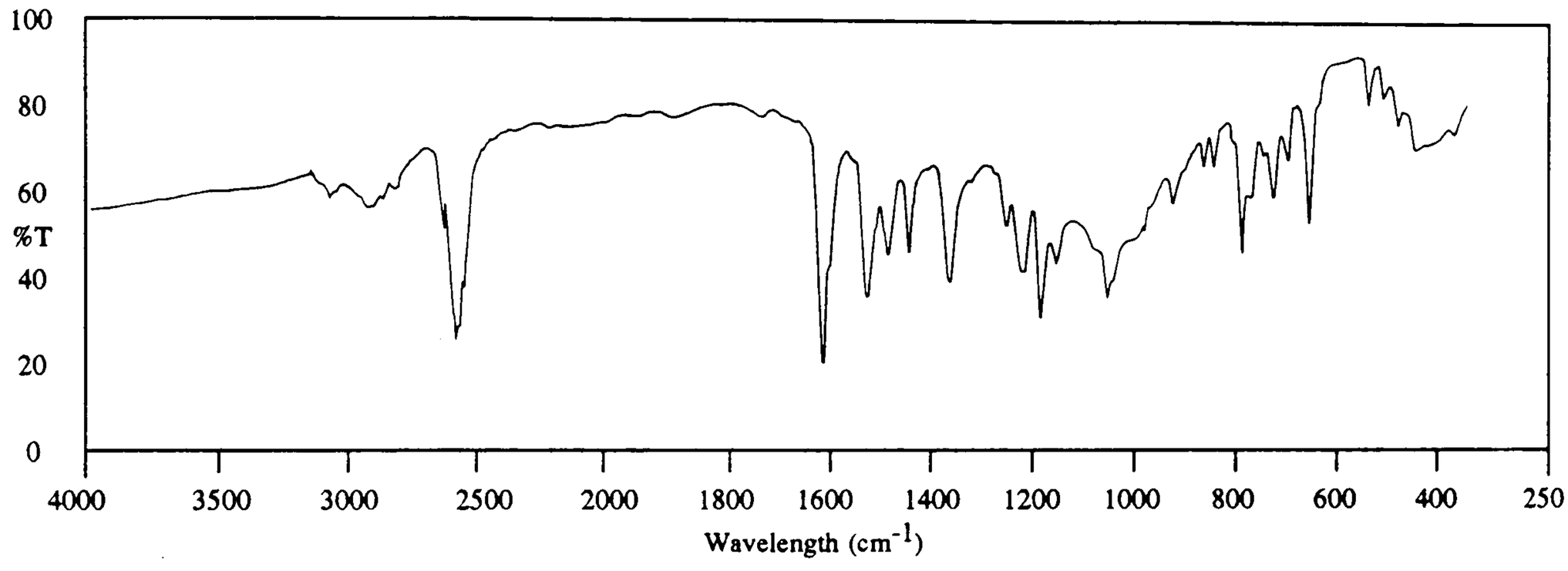


A solution of 3.32g (0.015 moles) of 4-N,N-dimethylaminodiphenylacetylene in 40ml anhydrous toluene was added to a slurry of 3.03g (0.015 moles) 6,9-bis(acetonitrile)-decaborane in 50ml dry toluene under nitrogen. The mixture was cautiously heated to reflux with hydrogen gas evolution and the solution turning red. After 26 hours refluxing, the dark red solution was cooled and diluted with 40ml methanol to remove any unreacted decaborane. After gas evolution ceased, the solvents were pumped off by rotary evaporator then *in vacuo*. The solid residue was crushed to a powder and extracted with boiling hexane. The extracts were combined and the hexane was removed leaving a pale green residue which was recrystallized from hexane to give 2.1g (41.3%) of yellow-green crystals identified as 1-phenyl-2-(4-N,N-dimethylaminophenyl)-*ortho*-carborane.

Melting point = 158-159°C

Analysis Found: C,57.0; H,7.1; N,3.8. $C_{16}H_{25}B_{10}N$ requires C,56.6; H,7.4; N,4.1.

Infrared (KBr disc; cm^{-1}) 3107(w), 3095(w), 3074(w), 3042(w), 2990(w), 2985(w), 2940(w), 2929(w), 2902(w), 2873(w), 2837(w), 2813(w), 2809(w), 2625(m), 2606(s), 2601(s), 2595(s), 2587(s), 2559(s), 1614(s), 1602(m), 1559(w), 1547(w), 1530(m), 1513(w), 1497(w), 1490(m), 1450(m), 1443(w), 1373(m), 1346(w), 1331(w), 1308(w), 1294(w), 1285(w), 1267(w), 1239(m), 1234(m), 1203(s), 1177(m), 1173(m), 1168(m), 1106(w), 1096(w), 1077(m), 1068(m), 1033(w), 1026(w), 1016(w), 1007(w), 951(w), 892(w), 862(w), 836(w), 820(m), 804(w), 777(w), 759(m), 730(w), 690(m), 574(w), 546(w), 518(w), 486(w), 479(w), 451(w), 413(w).



Ultraviolet (solvent MeOH, nm) 222(sharp), 288(broad), 310(shoulder).

Mass spectrum (E.I.) A highest mass peak was observed at m/e 341 corresponding to the species $^{12}C_{16}{}^{1}H_{25}{}^{11}B_{10}{}^{14}N$, accompanied by the usual carborane isotope distribution pattern between m/e 335 and 341.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

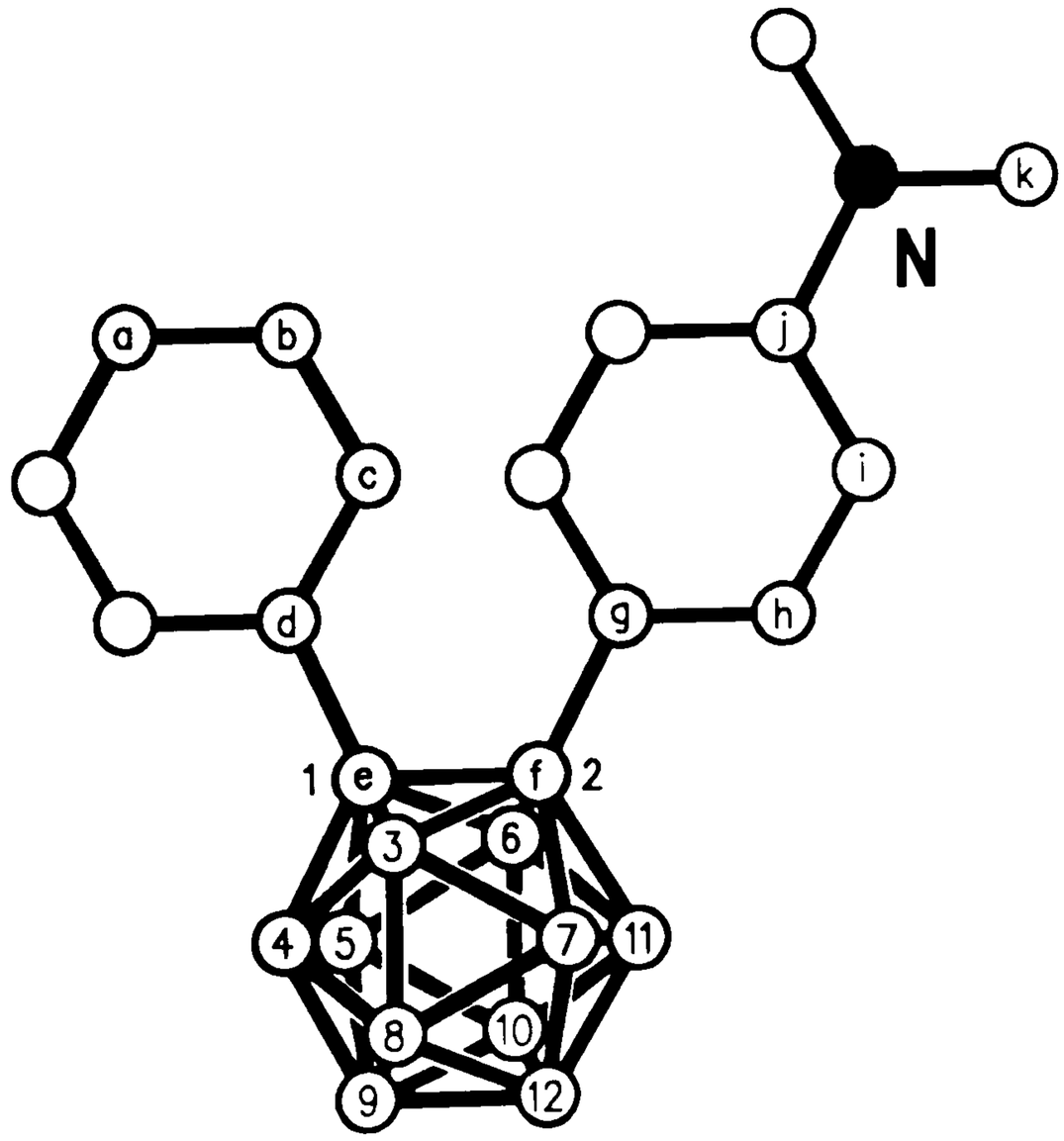
δ_{ppm}	intensity	type of peak	position of proton
8.00 7.97 6.91 6.88	4	doublet of doublets	aromatic C(h,i)-H
7.89-7.58	5	multiplet	aromatic C(a,b,c)-H
3.35	6	singlet	methyl C-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

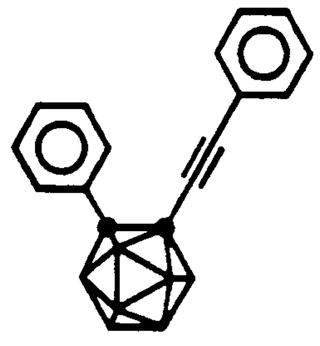
δ_{ppm}	intensity	position of boron
-2.91	2	9,12
-9.60	4	4,5,7,11
-11.14	4	3,6,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
151.05	j
131.62	h
130.71	c
129.87	a
128.14	b
119.22	g
110.99	i
87.74	f
85.85	e
39.93	k



1-phenyl-2-phenylethynyl-1,2-dicarba-*closo*-dodecaborane

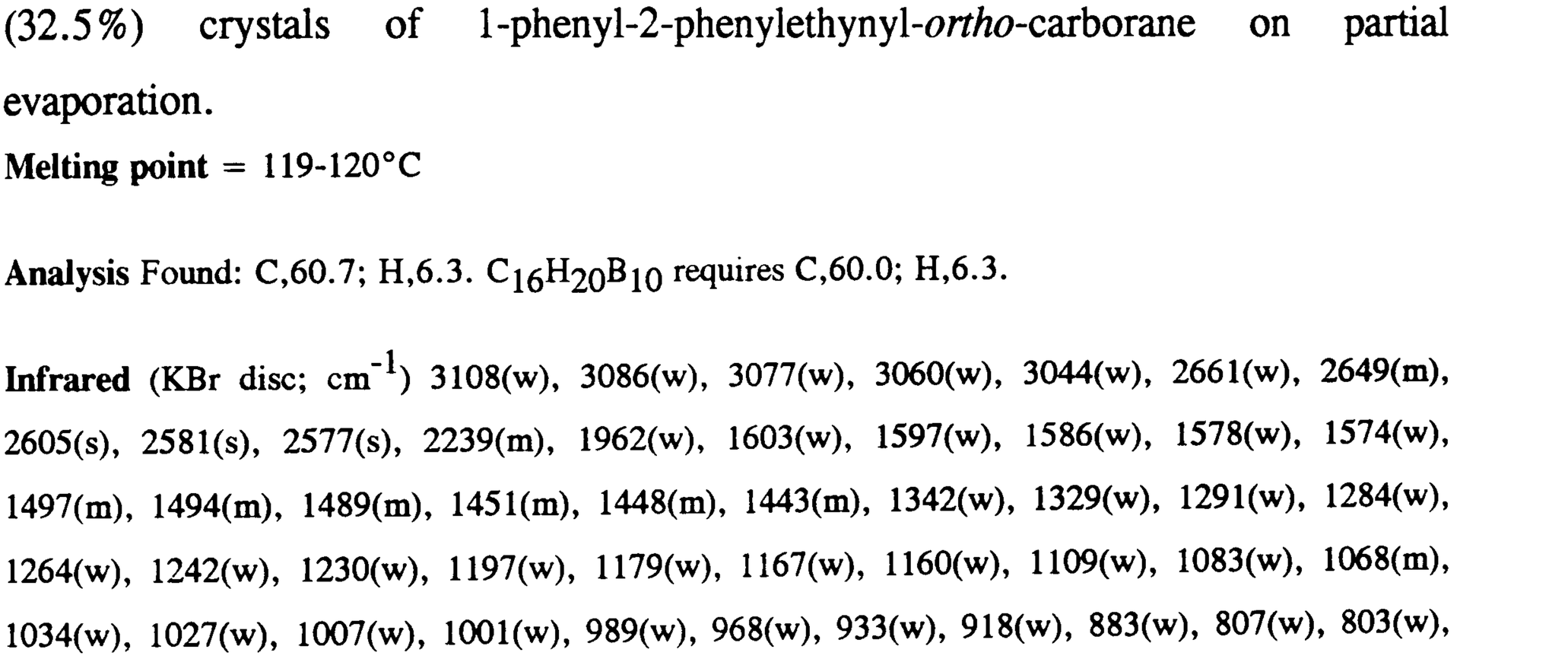


A solution of 1.01g (0.005 moles) 1,4-diphenylbutadiyne in 25ml dry toluene was added to a suspension of 1.01g (0.005 moles) 6,9-bis(acetonitrile) decaborane in 20ml toluene under nitrogen. The mixture was refluxed for 24 hours to give a red solution which was cooled then added with 20ml of methanol. The solvents were vacuum removed from the solution to leave a residue which was dissolved in hexane. The insoluble solid was filtered off and the filtrate gave 0.52g (32.5%) crystals of 1-phenyl-2-phenylethynyl-*ortho*-carborane on partial evaporation.

Melting point = 119-120°C

Analysis Found: C,60.7; H,6.3. $C_{16}H_{20}B_{10}$ requires C,60.0; H,6.3.

Infrared (KBr disc; cm^{-1}) 3108(w), 3086(w), 3077(w), 3060(w), 3044(w), 2661(w), 2649(m), 2605(s), 2581(s), 2577(s), 2239(m), 1962(w), 1603(w), 1597(w), 1586(w), 1578(w), 1574(w), 1497(m), 1494(m), 1489(m), 1451(m), 1448(m), 1443(m), 1342(w), 1329(w), 1291(w), 1284(w), 1264(w), 1242(w), 1230(w), 1197(w), 1179(w), 1167(w), 1160(w), 1109(w), 1083(w), 1068(m), 1034(w), 1027(w), 1007(w), 1001(w), 989(w), 968(w), 933(w), 918(w), 883(w), 807(w), 803(w), 777(w), 756(s), 737(w), 727(w), 687(s), 676(w), 636(w), 574(w), 520(m), 508(w), 488(w), 459(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 322 corresponding to the species $^{12}C_{16}{}^{1}H_{20}{}^{11}B_{10}$, accompanied by the usual carborane isotope distribution pattern between m/e 316 and 322.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

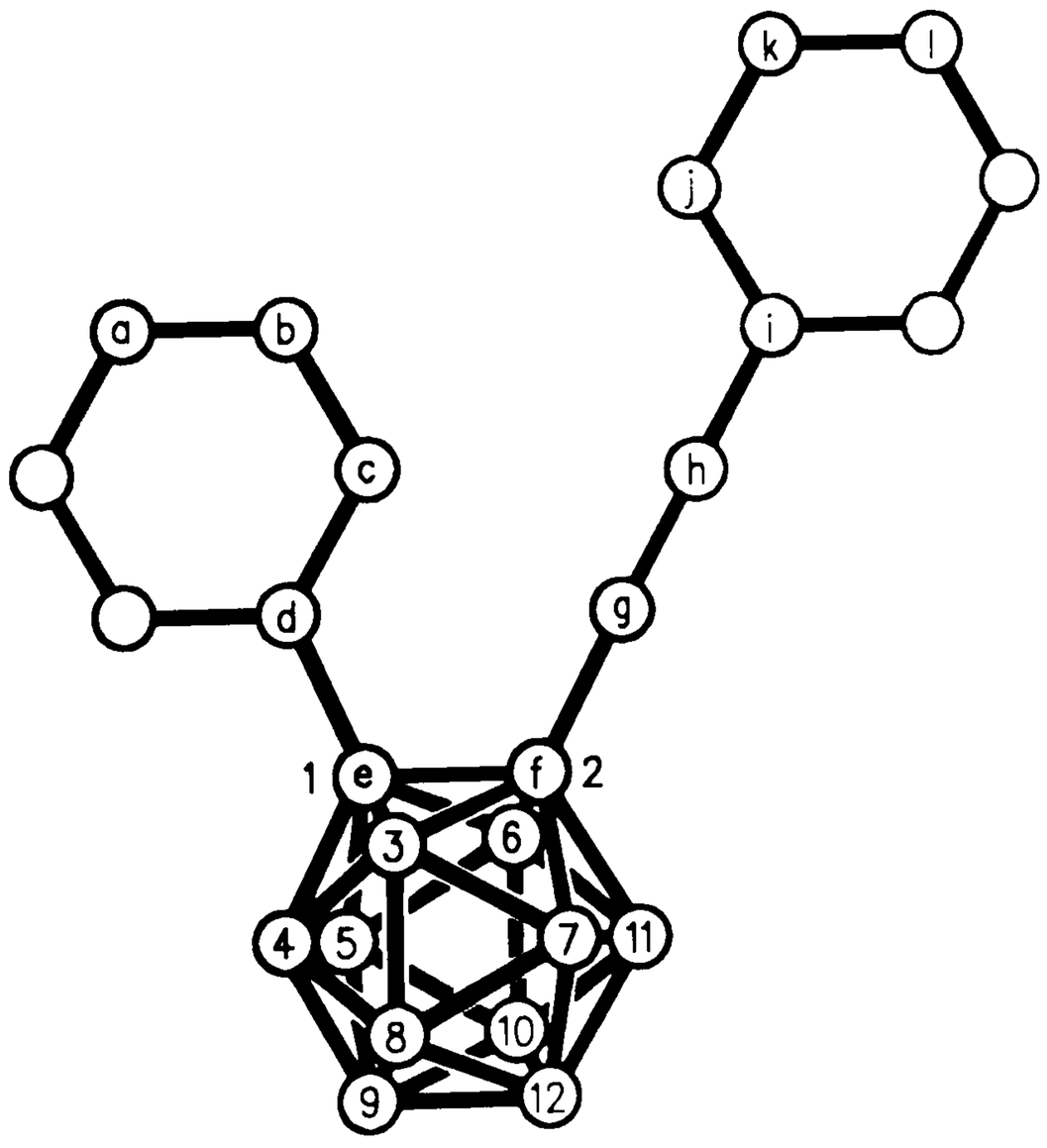
δ_{ppm}	intensity	type of peak	position of proton
7.78-7.00	10	multiplet	aromatic C-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-2.34	1	12
-4.07	1	9
-10.04	8	3,6,4,5,7,11,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
132.47	d
131.83	j
131.07	b
130.55	l
129.65	a
128.44	k
128.29	c
119.97	i
85.40	h
82.45	g
82.06	e
69.64	f



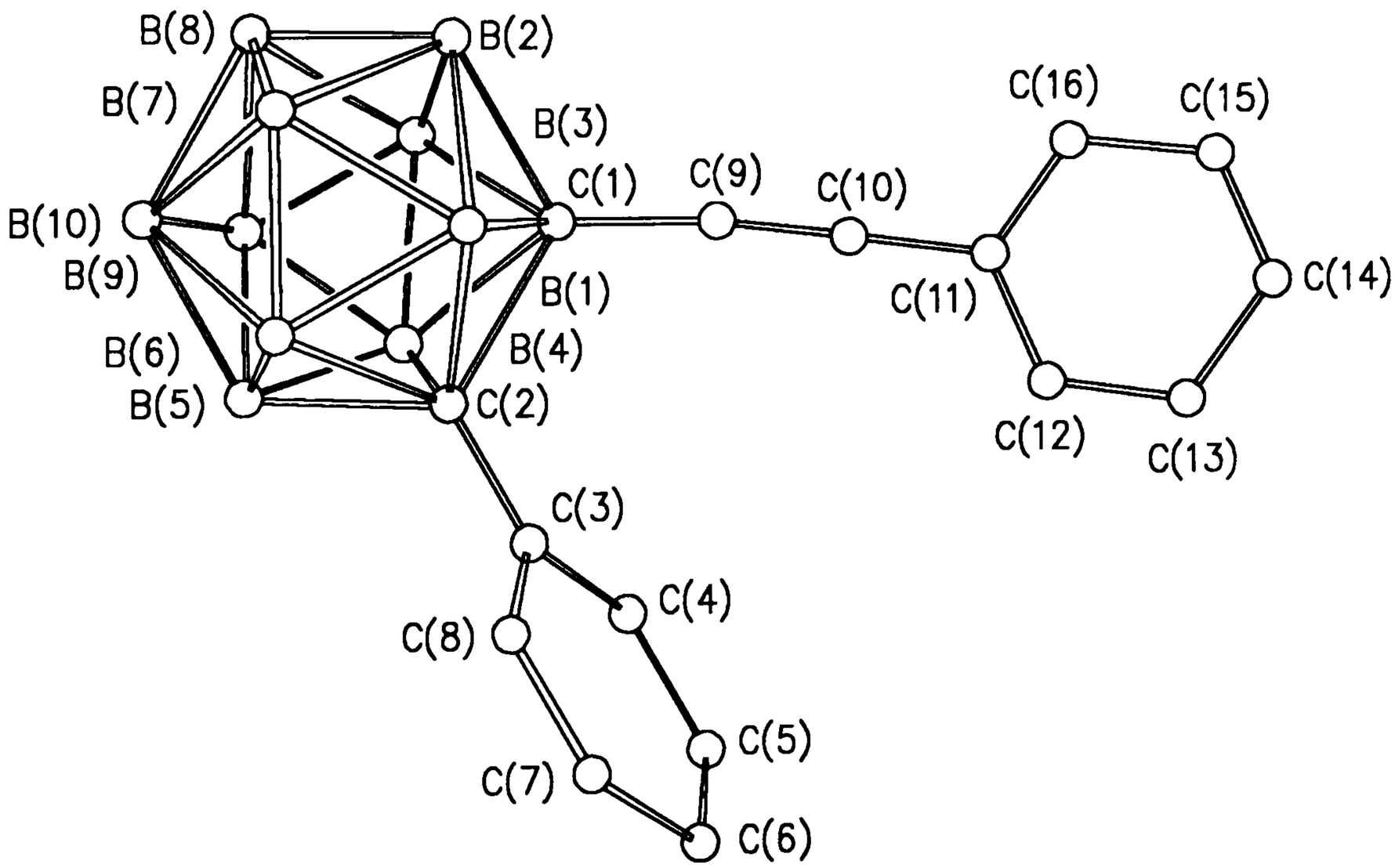
X-ray Analysis (W. Clegg, Newcastle University)

Crystallographic data, CuK_α radiation

Formula = $C_{16}H_{20}B_{10}$
Formula weight, M_r = 320.4
System = triclinic
Space Group = $P\bar{1}$
a = 7.283(1)Å
b = 10.412(1)Å
c = 12.763(2)Å
α = 74.34(1)°
β = 81.42(1)°
γ = 86.17(1)°
Unit cell volume, V = 921.12Å^3
Calculated density, D_c = 1.155gcm^{-3}
Number of formulae per cell, Z = 2
Absorption coefficient, μ = 0.38mm^{-1}
F(000) = 332 electrons

Number of unique reflections = 3082
Observed reflections, $F > 4\sigma_c(F)$ = 2807
$2\theta_{max}$ = 130°
Range, 2θ = 40 to 55°
Range, h = -8 to 8
Range, k = -12 to 12
Range, l = 0 to 14

Measure of overall precision of data, R_{sigma} = 0.010
Crystal size = 0.24 x 0.44 x 0.68
Crystal colour = colourless
Temperature, T = 240°K



Bond lengths (Å)

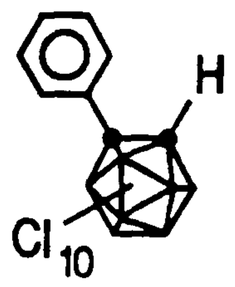
C(1)-C(2)	1.711(2)		C(1)-C(9)	1.430(2)
C(1)-B(1)	1.731(2)		C(1)-B(2)	1.706(2)
C(1)-B(3)	1.704(2)		C(1)-B(4)	1.724(2)
C(2)-C(3)	1.501(2)		C(2)-B(1)	1.741(2)
C(2)-B(4)	1.743(2)		C(2)-B(5)	1.707(2)
C(2)-B(6)	1.709(2)		C(3)-C(4)	1.392(2)
C(3)-C(8)	1.393(2)		C(4)-C(5)	1.382(2)
C(5)-C(6)	1.381(2)		C(6)-C(7)	1.378(2)
C(7)-C(8)	1.384(2)		C(9)-C(10)	1.199(2)
C(10)-C(11)	1.429(2)		C(11)-C(12)	1.390(2)
C(11)-C(16)	1.394(2)		C(12)-C(13)	1.388(3)
C(13)-C(14)	1.382(3)		C(14)-C(15)	1.365(2)
C(15)-C(16)	1.375(3)		B(1)-H(1)	1.060(19)
B(1)-B(2)	1.779(2)		B(1)-B(6)	1.770(2)
B(1)-B(7)	1.759(2)		B(2)-H(2)	1.078(20)
B(2)-B(3)	1.778(2)		B(2)-B(7)	1.779(3)
B(2)-B(8)	1.770(3)		B(3)-H(3)	1.074(18)
B(3)-B(4)	1.782(2)		B(3)-B(8)	1.773(3)
B(3)-B(9)	1.773(3)		B(4)-H(4)	1.086(15)
B(4)-B(5)	1.777(2)		B(4)-B(9)	1.758(2)
B(5)-H(5)	1.050(16)		B(5)-B(6)	1.783(2)
B(5)-B(9)	1.777(2)		B(5)-B(10)	1.774(2)
B(6)-H(6)	1.121(18)		B(6)-B(7)	1.776(2)
B(6)-B(10)	1.780(2)		B(7)-H(7)	1.061(16)
B(7)-B(8)	1.785(2)		B(7)-B(10)	1.781(2)
B(8)-H(8)	1.073(17)		B(8)-B(9)	1.784(2)
B(8)-B(10)	1.780(2)		B(9)-H(9)	1.077(19)
B(9)-B(10)	1.787(2)		B(10)-H(10)	1.114(20)

Bond angles (°)

C(2)-C(1)-C(9)	115.0(1)		C(2)-C(1)-B(1)	60.8(1)
C(9)-C(1)-B(1)	116.4(1)		C(2)-C(1)-B(2)	111.0(1)
C(9)-C(1)-B(2)	123.4(1)		C(2)-C(1)-B(2)	62.3(1)
C(2)-C(1)-B(3)	111.3(1)		C(9)-C(1)-B(3)	123.2(1)
B(1)-C(1)-B(3)	114.0(1)		B(2)-C(1)-B(3)	62.9(1)
C(2)-C(1)-B(4)	61.0(1)		C(9)-C(1)-B(4)	116.1(1)
B(1)-C(1)-B(4)	113.0(1)		B(2)-C(1)-B(4)	114.2(1)
B(3)-C(1)-B(4)	62.7(1)		C(1)-C(2)-C(3)	117.6(1)
C(1)-C(2)-B(1)	60.2(1)		C(3)-C(2)-B(1)	119.5(1)
C(1)-C(2)-B(4)	59.9(1)		C(3)-C(2)-B(4)	115.4(1)
B(1)-C(2)-B(4)	111.5(1)		C(1)-C(2)-B(5)	109.0(1)
C(3)-C(2)-B(5)	121.9(1)		B(1)-C(2)-B(5)	112.8(1)
B(4)-C(2)-B(5)	62.0(1)		C(1)-C(2)-B(6)	109.2(1)
C(3)-C(2)-B(6)	124.3(1)		B(1)-C(2)-B(6)	61.7(1)
B(4)-C(2)-B(6)	113.2(1)		B(5)-C(2)-B(6)	62.9(1)
C(2)-C(3)-C(4)	122.1(1)		C(2)-C(3)-C(8)	119.6(1)
C(4)-C(3)-C(8)	118.3(1)		C(3)-C(4)-C(5)	120.5(1)
C(4)-C(5)-C(6)	120.7(1)		C(5)-C(6)-C(7)	119.4(1)
C(6)-C(7)-C(8)	120.3(1)		C(3)-C(8)-C(7)	120.8(1)
C(1)-C(9)-C(10)	174.5(1)		C(9)-C(10)-C(11)	178.2(1)
C(10)-C(11)-C(12)	119.9(1)		C(10)-C(11)-C(16)	120.0(1)
C(12)-C(11)-C(16)	120.1(1)		C(11)-C(12)-C(13)	119.1(2)
C(12)-C(13)-C(14)	120.1(1)		C(13)-C(14)-C(15)	120.5(2)
C(14)-C(15)-C(16)	120.5(2)		C(11)-C(16)-C(15)	119.7(1)
C(1)-B(1)-C(2)	59.0(1)		C(1)-B(1)-H(1)	117.9(10)
C(2)-B(1)-H(1)	117.7(8)		C(1)-B(1)-B(2)	58.2(1)
C(2)-B(1)-B(2)	106.2(1)		H(1)-B(1)-B(2)	123.3(9)
C(1)-B(1)-B(6)	105.6(1)		C(2)-B(1)-B(6)	58.2(1)
H(1)-B(1)-B(6)	124.1(10)		B(2)-B(1)-B(6)	108.7(1)
C(1)-B(1)-B(7)	105.0(1)		C(2)-B(1)-B(7)	105.6(1)
H(1)-B(1)-B(7)	129.9(9)		B(2)-B(1)-B(7)	60.4(1)
B(6)-B(1)-B(7)	60.4(1)		C(1)-B(2)-B(1)	59.5(1)
C(1)-B(2)-H(2)	115.1(10)		B(1)-B(2)-H(2)	120.1(10)
C(1)-B(2)-B(3)	58.5(1)		B(1)-B(2)-B(3)	108.1(1)
H(2)-B(2)-B(3)	116.4(9)		C(1)-B(2)-B(7)	105.2(1)
B(1)-B(2)-B(7)	59.3(1)		H(2)-B(2)-B(7)	130.6(9)
B(3)-B(2)-B(7)	108.3(1)		C(1)-B(2)-B(8)	104.9(1)
B(1)-B(2)-B(8)	107.6(1)		H(2)-B(2)-B(8)	128.4(10)
B(3)-B(2)-B(8)	60.0(1)		B(7)-B(2)-B(8)	60.4(1)
C(1)-B(3)-B(2)	58.6(1)		C(1)-B(3)-H(3)	118.2(11)
B(2)-B(3)-H(3)	122.5(10)		C(1)-B(3)-B(4)	59.2(1)
B(2)-B(3)-B(4)	107.9(1)		H(3)-B(3)-B(4)	116.5(8)
C(1)-B(3)-B(8)	104.8(1)		B(2)-B(3)-B(8)	59.8(1)
H(3)-B(3)-B(8)	129.4(9)		B(4)-B(3)-B(8)	107.6(1)
C(1)-B(3)-B(9)	105.0(1)		B(2)-B(3)-B(9)	108.1(1)
H(3)-B(3)-B(9)	125.1(11)		B(4)-B(3)-B(9)	59.3(1)
B(8)-B(3)-B(9)	60.4(1)		C(1)-B(4)-C(2)	59.1(1)
C(1)-B(4)-B(3)	58.1(1)		C(2)-B(4)-B(3)	106.1(1)
C(1)-B(4)-H(4)	116.8(10)		C(2)-B(4)-H(4)	117.6(9)
B(3)-B(4)-H(4)	122.8(8)		C(1)-B(4)-B(5)	105.3(1)
C(2)-B(4)-B(5)	58.0(1)		B(3)-B(4)-B(5)	108.3(1)
H(4)-B(4)-B(5)	125.4(9)		C(1)-B(4)-B(9)	104.7(1)
C(2)-B(4)-B(9)	105.3(1)		B(3)-B(4)-B(9)	60.1(1)
H(4)-B(4)-B(9)	130.9(10)		B(5)-B(4)-B(9)	60.3(1)
C(2)-B(5)-B(4)	60.0(1)		C(2)-B(5)-H(5)	115.3(10)

B(4)-B(5)-H(5)	118.8(9)	C(2)-B(5)-B(6)	58.6(1)
B(4)-B(5)-B(6)	108.2(1)	H(5)-B(5)-B(6)	118.5(9)
C(2)-B(5)-B(9)	106.1(1)	B(4)-B(5)-B(9)	59.3(1)
H(5)-B(5)-B(9)	128.6(9)	B(6)-B(5)-B(9)	108.3(1)
C(2)-B(5)-B(10)	105.7(1)	B(4)-B(5)-B(10)	107.8(1)
H(5)-B(5)-B(10)	128.6(10)	B(6)-B(5)-B(10)	60.0(1)
B(9)-B(5)-B(10)	60.4(9)	C(2)-B(6)-B(1)	60.0(1)
C(2)-B(6)-B(5)	58.5(1)	B(1)-B(6)-B(5)	107.9(1)
C(2)-B(6)-H(6)	116.4(9)	B(1)-B(6)-H(6)	116.9(10)
B(5)-B(6)-H(6)	121.6(8)	C(2)-B(6)-B(7)	106.2(1)
B(1)-B(6)-B(7)	59.5(1)	B(5)-B(6)-B(7)	107.9(1)
H(6)-B(6)-B(7)	126.2(8)	C(2)-B(6)-B(10)	105.3(1)
B(1)-B(6)-B(10)	107.5(1)	B(5)-B(6)-B(10)	59.7(1)
H(6)-B(6)-B(10)	129.7(10)	B(7)-B(6)-B(10)	60.1(1)
B(1)-B(7)-B(2)	60.4(1)	B(1)-B(7)-B(6)	60.1(1)
B(2)-B(7)-B(6)	108.4(1)	B(1)-B(7)-H(7)	118.3(11)
B(2)-B(7)-H(7)	120.4(11)	B(6)-B(7)-H(7)	120.6(9)
B(1)-B(7)-B(8)	107.9(1)	B(2)-B(7)-B(8)	59.6(1)
B(6)-B(7)-B(8)	108.0(1)	H(7)-B(7)-B(8)	124.5(10)
B(1)-B(7)-B(10)	107.9(1)	B(2)-B(7)-B(10)	107.7(1)
B(6)-B(7)-B(10)	60.0(1)	H(7)-B(7)-B(10)	124.7(12)
B(8)-B(7)-B(10)	59.9(1)	B(2)-B(8)-B(3)	60.2(1)
B(2)-B(8)-B(7)	60.0(1)	B(3)-B(8)-B(7)	108.3(1)
B(2)-B(8)-H(8)	121.3(11)	B(3)-B(8)-H(8)	120.4(10)
B(7)-B(8)-H(8)	122.6(9)	B(2)-B(8)-B(9)	107.9(1)
B(3)-B(8)-B(9)	59.8(1)	B(7)-B(8)-B(9)	108.0(1)
H(8)-B(8)-B(9)	121.4(10)	B(2)-B(8)-B(10)	108.1(1)
B(3)-B(8)-B(10)	108.2(1)	B(7)-B(8)-B(10)	60.0(1)
H(8)-B(8)-B(10)	122.5(11)	B(9)-B(8)-B(10)	60.2(1)
B(3)-B(9)-B(4)	60.6(1)	B(3)-B(9)-B(5)	108.7(1)
B(4)-B(9)-B(5)	60.3(1)	B(3)-B(9)-B(8)	59.8(1)
B(4)-B(9)-B(8)	108.2(1)	B(5)-B(9)-B(8)	107.8(1)
B(3)-B(9)-H(9)	118.8(10)	B(4)-B(9)-H(9)	121.1(9)
B(5)-B(9)-H(9)	124.1(9)	B(8)-B(9)-H(9)	120.5(8)
B(3)-B(9)-B(10)	107.9(1)	B(4)-B(9)-B(10)	108.1(1)
B(5)-B(9)-B(10)	59.7(1)	B(8)-B(9)-B(10)	59.8(1)
H(9)-B(9)-B(10)	123.6(11)	B(5)-B(10)-B(6)	60.2(1)
B(5)-B(10)-B(7)	108.1(1)	B(6)-B(10)-B(7)	59.8(1)
B(5)-B(10)-B(8)	108.1(1)	B(6)-B(10)-B(8)	108.1(1)
B(7)-B(10)-B(8)	60.2(1)	B(5)-B(10)-B(9)	59.9(1)
B(6)-B(10)-B(9)	108.0(1)	B(7)-B(10)-B(9)	108.0(1)
B(8)-B(10)-B(9)	60.0(1)	B(5)-B(10)-H(10)	117.9(8)
B(6)-B(10)-H(10)	116.6(9)	B(7)-B(10)-H(10)	122.1(9)
B(8)-B(10)-H(10)	127.0(8)	B(9)-B(10)-H(10)	124.4(9)

1-phenyl-3,4,5,6,7,8,9,10,11,12-decachloro-1,2-dicarba-*closo*-dodecaborane

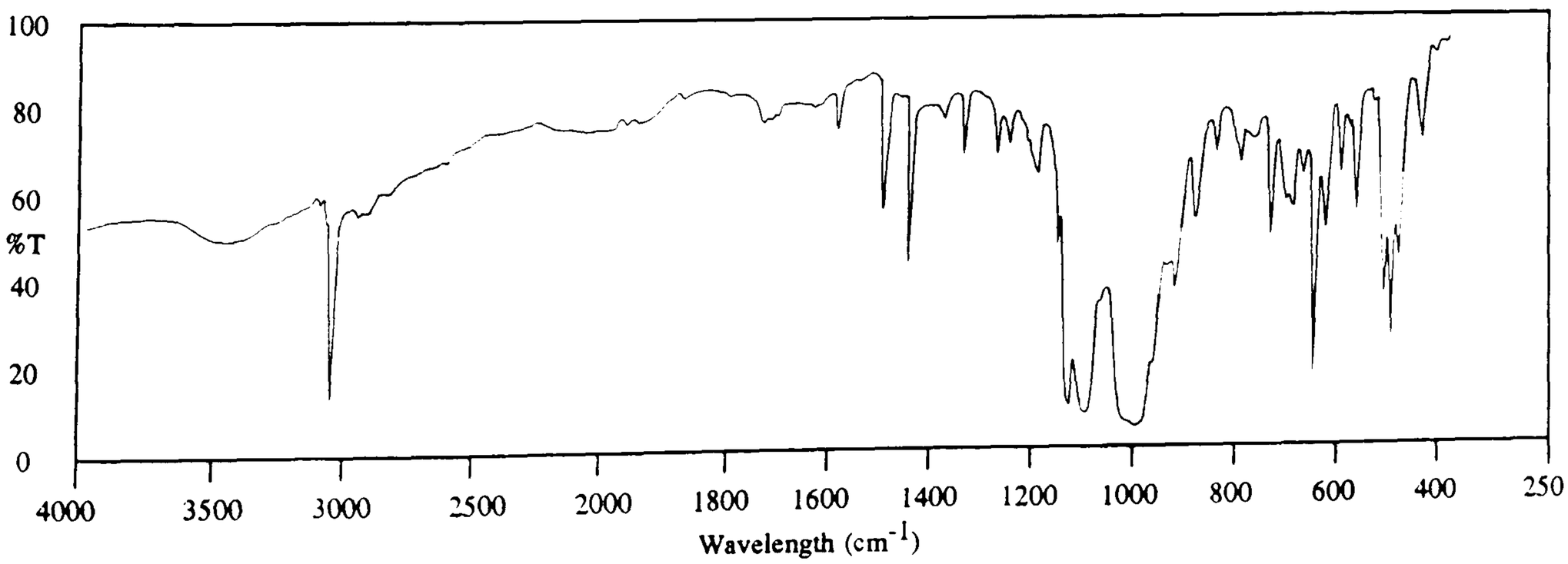


In a well ventilated fume cupboard, chlorine gas was bubbled through a solution of 2.2g (0.01 moles) of 1-phenyl-*ortho*-carborane in 40ml carbon tetrachloride with stirring. It was left stirring under a Hanovia UV51000 ultraviolet lamp for 36 hours. The cloudy orange solution was filtered, the filtrate was vacuum-evaporated and the residue was recrystallized from hexane to give 2.1g (37.2%) of 1-phenyl-3,4,5,6,7,8,9,10,11,12-decachloro-*ortho*-carborane.

Melting point = 231-232°C (lit[29]. = 240-241°C)

Analysis Found: C,17.0; H,1.1; B,19.1; Cl,62.8. $C_8H_6B_{10}Cl_{10}$ requires C,17.0; H,1.1; B,18.0; Cl,63.9.

Infrared (KBr disc; cm^{-1}) 3106(w), 3077(w), 3052(s), 2962(w), 2930(w), 2855(w), 1588(w), 1503(m), 1452(m), 1388(w), 1349(w), 1288(w), 1266(w), 1231(w), 1212(w), 1173(m), 1151(s), 1120(s), 1041(s), 1022(s), 995(s), 964(m), 947(m), 908(m), 868(w), 824(w), 801(w), 764(m), 736(w), 722(m), 703(w), 682(s), 660(m), 630(w), 616(w), 600(m), 567(w), 548(m), 533(m), 518(m), 474(w), 448(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 572 corresponding to the species $^{12}C_8{}^{1}H_6{}^{11}B_{10}{}^{35}Cl_5{}^{37}Cl_5$, accompanied by the boron and chlorine isotope distribution pattern between m/e 556 and 572.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

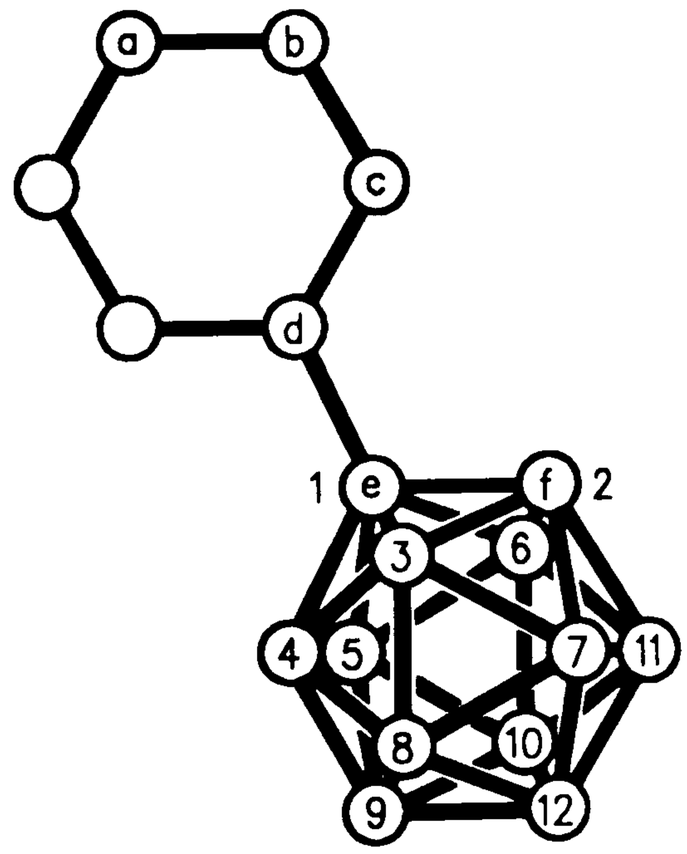
δ_{ppm}	intensity	type of peak	position of proton
7.82-7.58	5	multiplet	aromatic C(a,b,c)-H
4.82	1	broad singlet	carboranyl C(f)-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

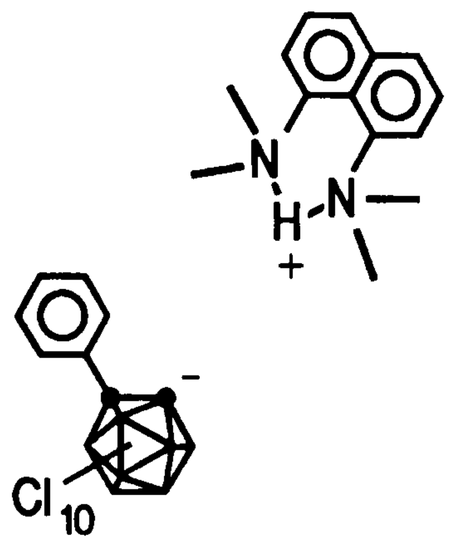
δ_{ppm}	intensity	position of boron
1.63	2	3,6
-6.31	2	4,5
-8.54	2	7,11
-10.08	4	8,10,9,12

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
132.35	c
129.63	a
129.48	b
120.63	d
56.35	e
45.13	f



Proton sponge adduct of 1-phenyl-3,4,5,6,7,8,9,10,11,12-decachloro-1,2-dicarba-*closo*-dodecaborane

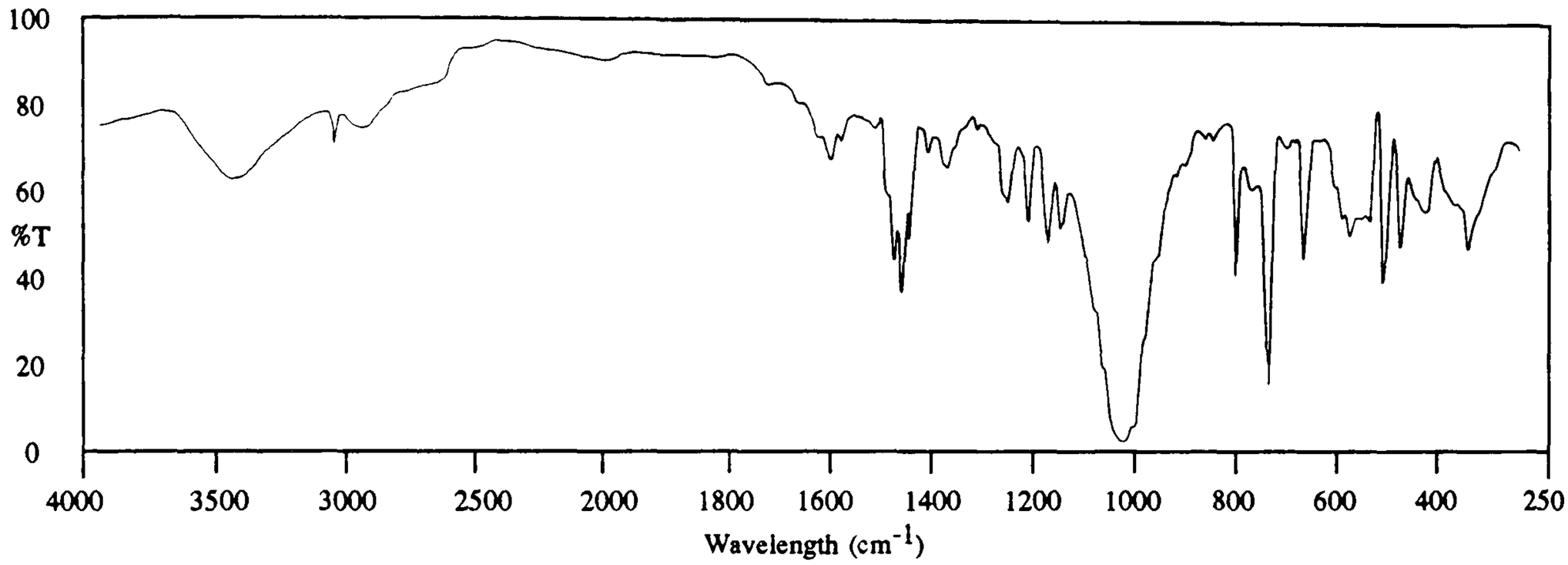


A solution of 0.565g (0.001 moles) 1-phenyl-3,4,5,6,7,8,9,10,11,12-decachloro-*ortho*-carborane in 10ml hexane was poured into a solution of 0.214g (0.001 moles) proton sponge in 10ml hexane. A white precipitate immediately appeared which was filtered off and washed with fresh hexane to give 0.717g (92.0%) of 1:1 proton sponge : 1-phenyl-3,4,5,6,7,8,9,10,11,12-decachloro-*ortho*-carborane adduct.

Melting point = over 320°C

Analysis Found: C,33.2; H,3.1; N,3.0; B,13.9; Cl,45.6. $C_{22}H_{24}B_{10}Cl_{10}N_2$ requires C,33.8; H,3.1; N,3.6; B,12.1; Cl,41.8.

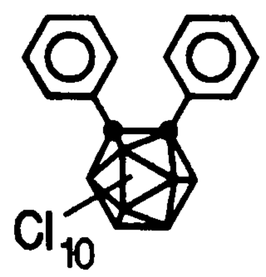
Infrared (KBr disc; cm^{-1}) 3625-3100(m,br), 3069(w), 3059(w), 2952(w), 1625(w), 1600(w), 1583(w), 1517(w), 1511(w), 1487(w), 1478(m), 1462(m), 1450(m), 1416(w), 1410(w), 1385(w), 1380(w), 1378(w), 1324(w), 1300(w), 1274(w), 1265(w), 1225(m), 1187(m), 1165(m), 1160(m), 1100(m), 1079(s), 1040(s), 1022(s), 1002(s), 982(w), 944(w), 931(w), 920(w), 894(w), 877(w), 829(m), 800(w), 766(s), 763(s), 737(w), 718(w), 698(m), 670(w), 639(w), 624(w), 610(w), 588(w), 572(w), 545(m), 521(m), 484(w), 470(w), 462(w), 428(w), 410(w), 382(m), 358(w), 331(w).



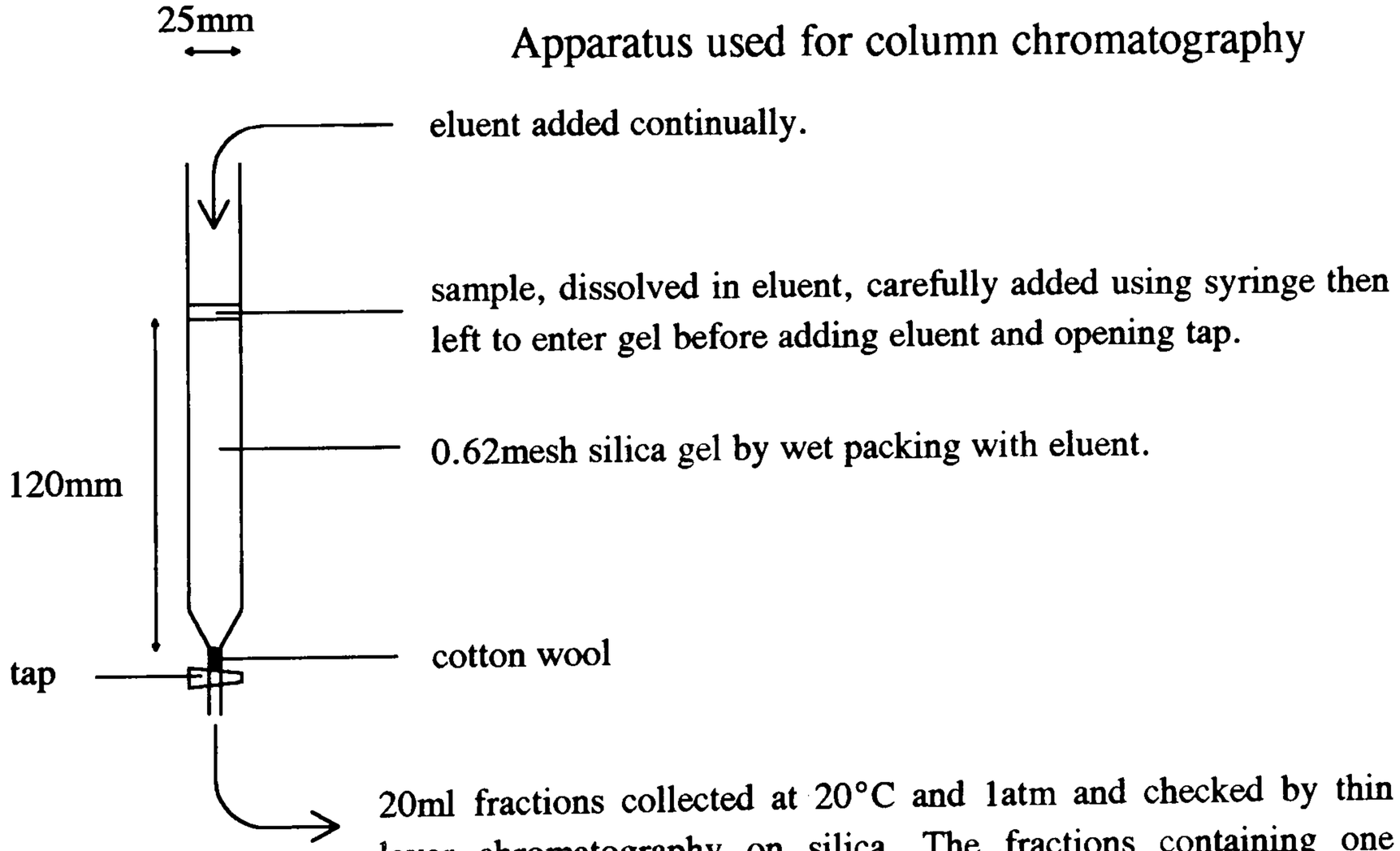
The insolubility of the adduct prevents use of solution state n.m.r. and X-ray analysis. Solid state n.m.r. was carried out instead.

^{13}C N.M.R. solid state M.A.S. 75.431 MHz; referenced externally to $(CH_3)_4Si$ at 0.00ppm. Poor spectrum was obtained and peaks were observed at 143.61, 135.68, 129.53, 122.69, 120.23 and 46.94. The cage carbon peaks may be hidden in the aromatic peaks.

1,2-diphenyl-3,4,5,6,7,8,9,10,11,12-decachloro-1,2-dicarba-*closo*-dodecaborane



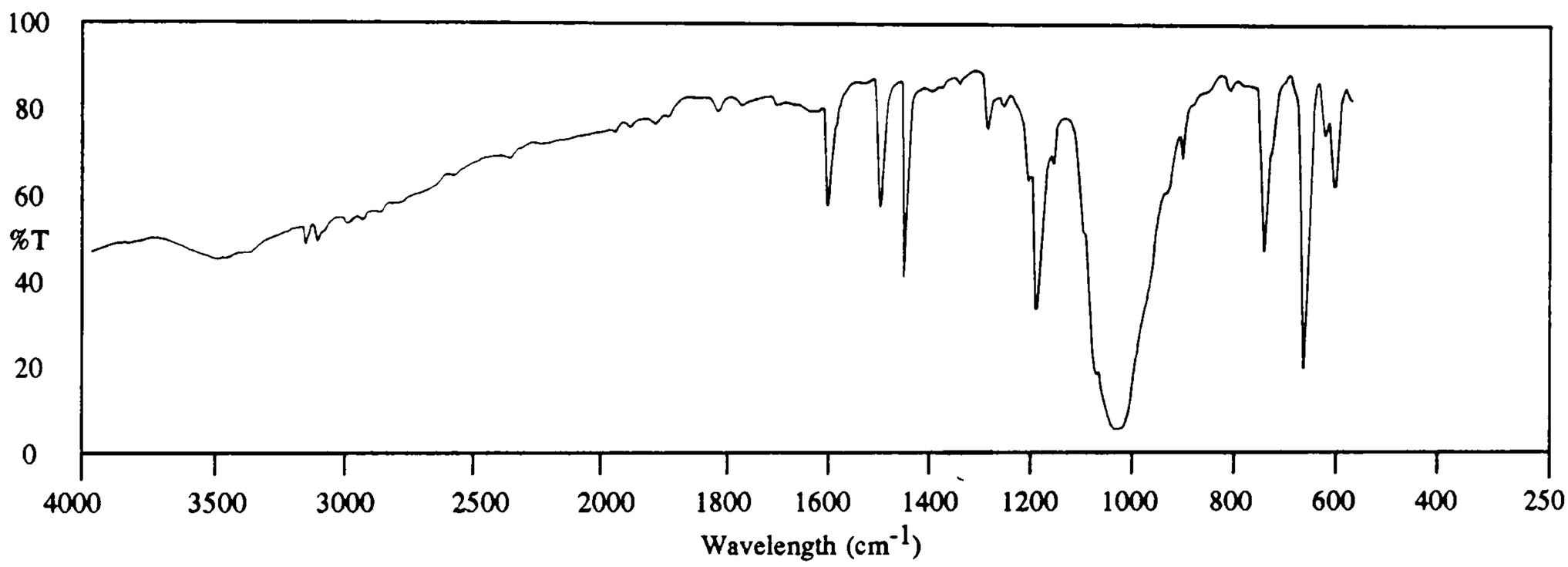
In a good fume cupboard, 2.96g (0.01 moles) of 1,2-diphenyl-*ortho*-carborane in 50ml carbon tetrachloride was saturated with chlorine gas bubbling through with stirring. The solution was left stirring under a Hanovia UV51000 ultraviolet lamp with chlorine gas passing at a slow rate for 48 hours. The cloudy orange solution was cooled and filtered. The filtrate was pumped to dryness using a rotary evaporator to yield a residue which was subjected to three runs of column chromatography with 1g of sample and carbon tetrachloride as eluent to give 1.22g (19.0%) of 1,2-diphenyl-3,4,5,6,7,8,9,10,11,12-decachloro-*ortho*-carborane.



Melting point = 272-273°C

Analysis Found: C,26.3; H,1.6; B,16.8. $C_{14}H_{10}B_{10}Cl_{10}$ requires C,26.2; H,1.6; B,16.9.

Infrared (KBr disc; cm^{-1}) 3124(w), 3080(w), 1800(w), 1592(m), 1492(m), 1446(m), 1394(w), 1379(w), 1344(w), 1291(w), 1258(w), 1212(w), 1197(m), 1167(w), 1108(m), 1082(s), 1045(s), 1033(s), 1007(s), 979(m), 953(w), 922(w), 906(w), 876(w), 832(w), 792(w), 768(m), 758(w), 690(s), 651(w), 631(w).



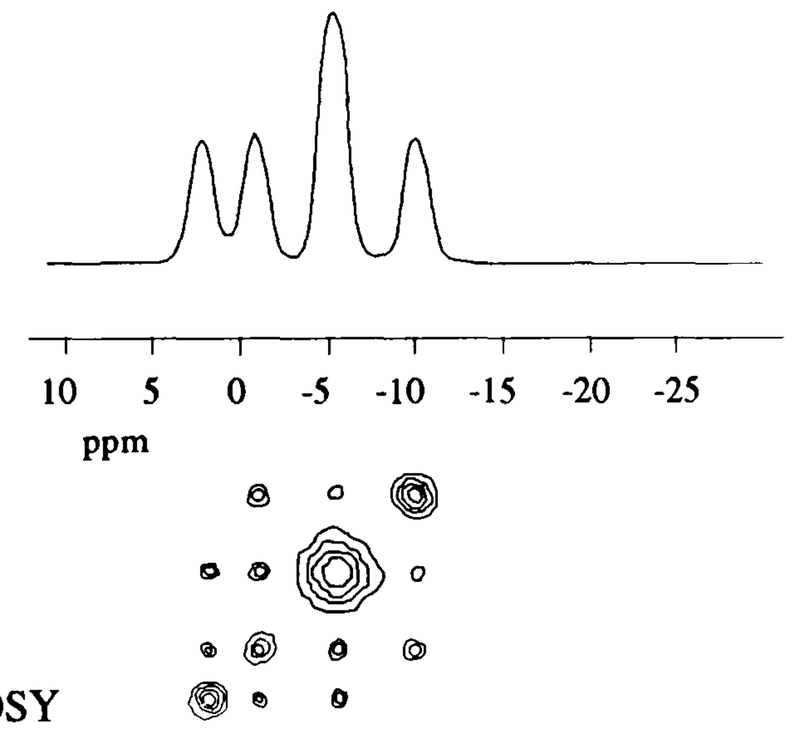
Mass spectrum (E.I.) A highest mass peak was observed at m/e 648 corresponding to the species $^{12}C_{14}{}^{1}H_{10}{}^{11}B_{10}{}^{35}Cl_5{}^{37}Cl_5$, accompanied by boron and chlorine isotope distribution pattern between m/e 634 and 648.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
8.12-7.98 7.70-7.32	10	multiplet	aromatic C(a,b,c)-H

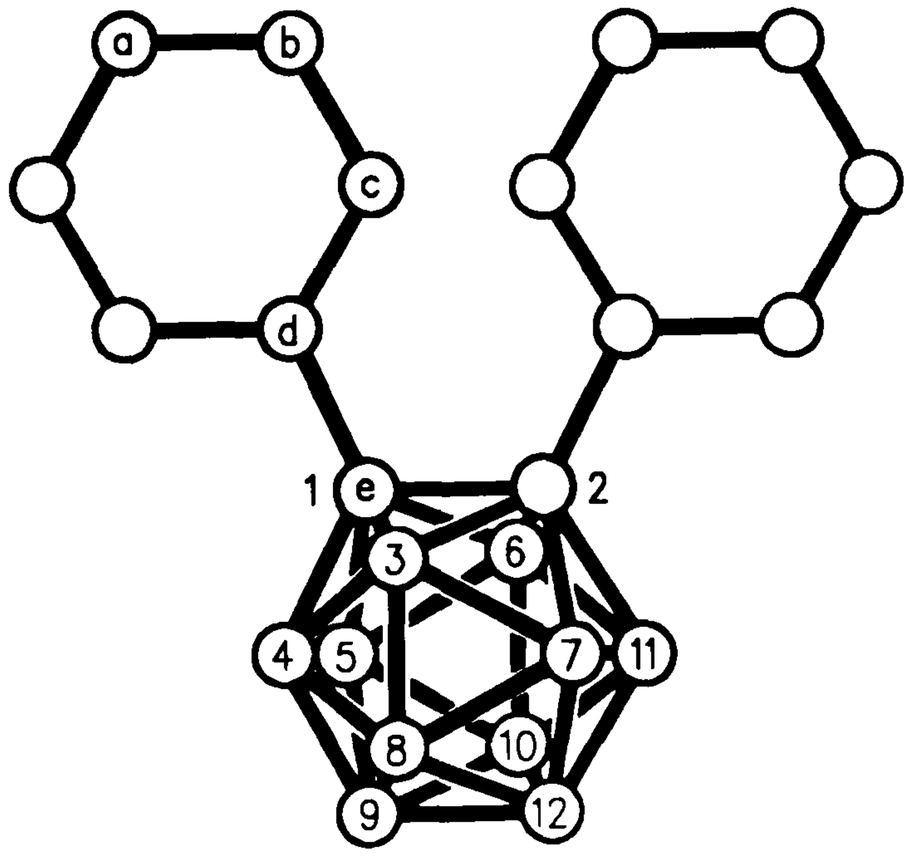
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
2.13	2	9,12
-0.94	2	8,10
-5.46	4	4,5,7,11
-10.07	2	3,6

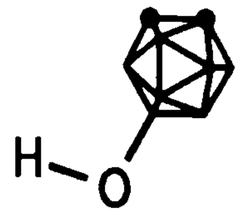


^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
133.05	a
132.34	c
129.03	b
124.81	d
77.39	e



9-hydroxy-1,2-dicarba-*closo*-dodecaborane

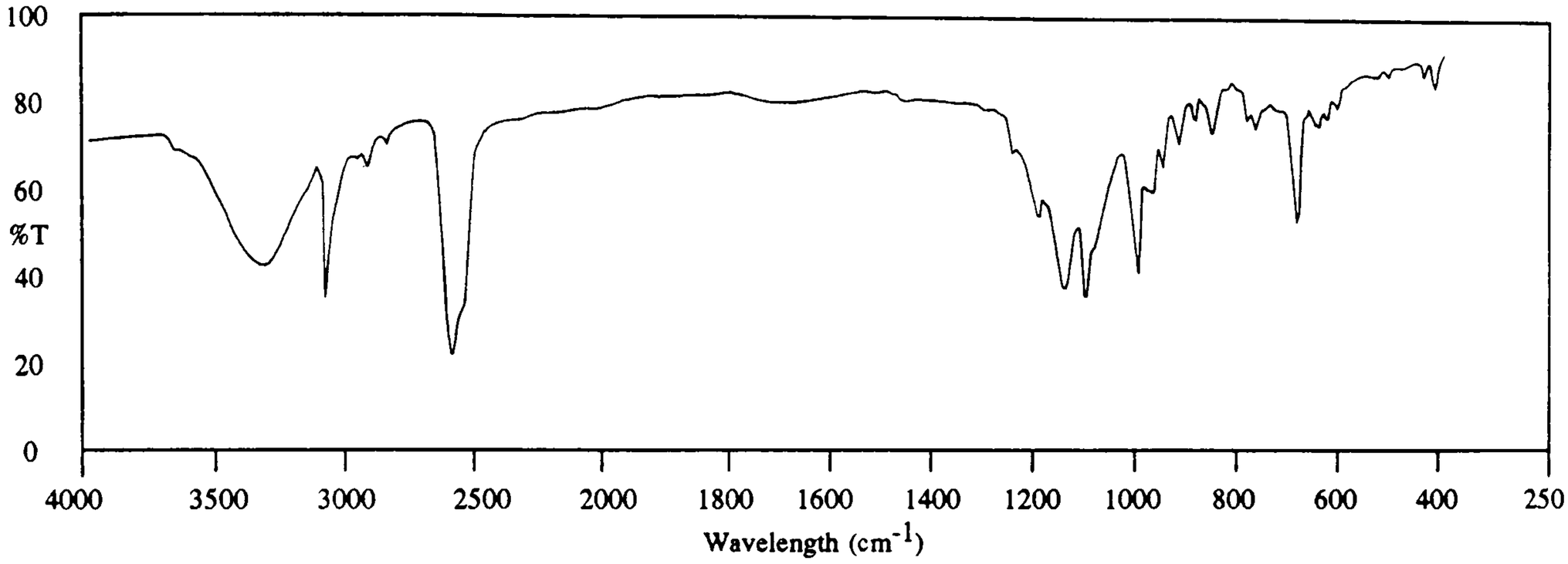


In a fume cupboard with an explosion screen, 7ml of fuming nitric acid was added very slowly to a solution of 1.44g (0.01 moles) *ortho*-carborane in 20ml carbon tetrachloride with stirring. After stirring for 4 hours, it was poured into 100ml of water and the undissolved solid was filtered off, washed with carbon tetrachloride and dissolved in diethyl ether. The ether solution was dried over magnesium sulphate and filtered. Ether was driven off by rotary evaporator to leave a residue which was recrystallized from a toluene : hexane mixture to give 0.11g (6.9%) of 9-hydroxy-*ortho*-carborane. The carbon tetrachloride filtrate was washed with sodium carbonate solution, water, dried over anhydrous magnesium sulphate and filtered. The solvent was pumped off by rotary evaporator to leave a mixture of unreacted *ortho*-carborane and 9-nitrato-*ortho*-carborane. This mixture was dissolved in 15ml of absolute alcohol with stirring, 5g tin powder and 8ml concentrated hydrochloric acid was added and refluxed for 3 hours. The alcohol was vacuum evaporated from the mixture to leave a residue which was extracted with water and carbon tetrachloride. The undissolved material was filtered off and recrystallized from a toluene : hexane mixture to give a further 0.22g (13.8%; total yield,20.7%) of 9-hydroxy-*ortho*-carborane.

Melting point = over 320°C (lit[39]. = 412-414°C)

Analysis Found: C,14.9; H,7.0. $C_2H_{12}B_{10}O$ requires C,15.0; H,7.5.

Infrared (KBr disc; cm^{-1}) 3690-3140(s,br), 3084(s), 2974(w), 2938(w), 2864(w), 2613(s), 2600(s), 2581(s), 2571(s), 1266(w), 1213(w), 1168(m), 1131(m), 1113(m), 1086(w), 1033(m), 1014(w), 1004(w), 983(w), 952(w), 923(w), 889(w), 825(w), 807(w), 768(w), 732(m), 728(m), 712(w), 696(w), 688(w), 672(w), 654(w), 580(w), 554(w), 485(w), 463(w).



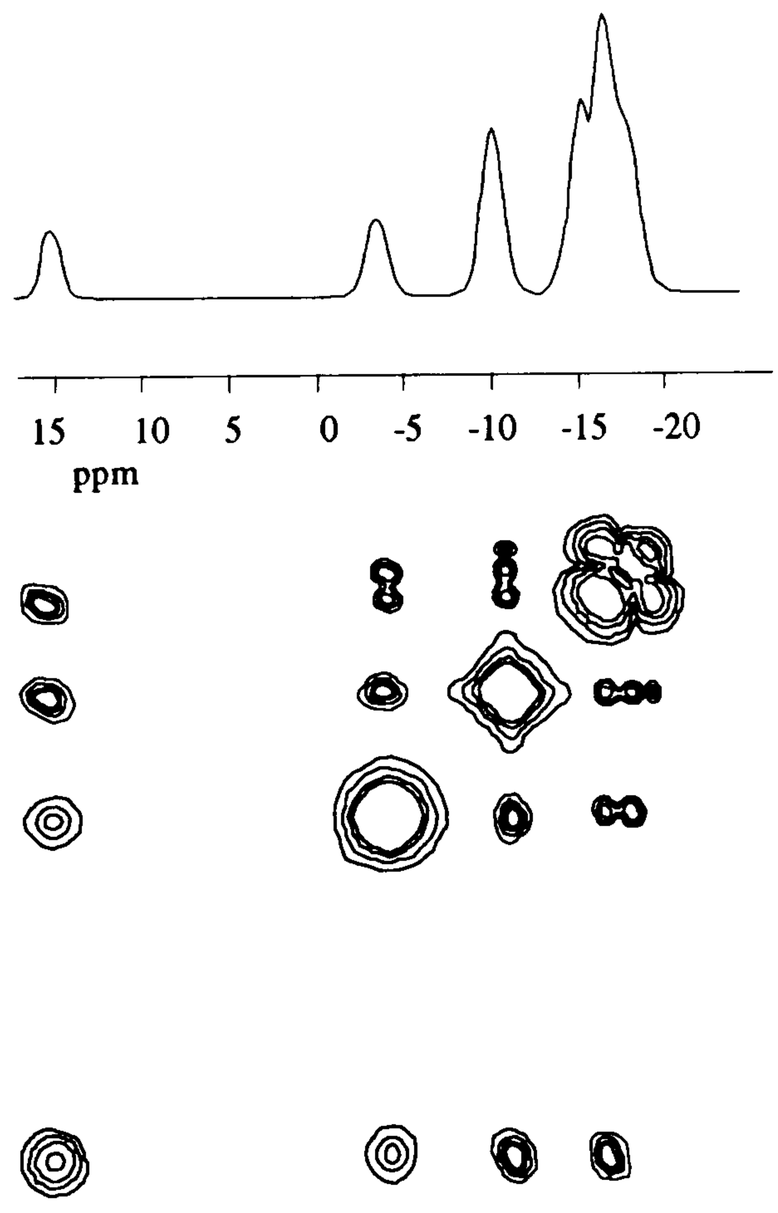
Mass spectrum (E.I.) A highest mass peak was observed at m/e 162 corresponding to the species $^{12}C_2{}^{1}H_{12}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 156 and 162.

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

δ_{ppm}	intensity	type of peak	position of proton
3.36	1	broad singlet	carboranyl C(a)-H
3.26	1	broad singlet	carboranyl C(b)-H
2.61	1	broad singlet	O-H
4.0-0.9	9	broad multiplet	carboranyl B-H

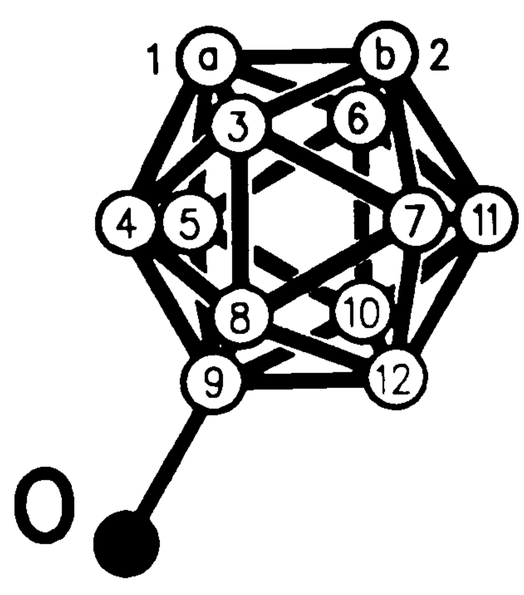
^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
15.23	1	9
-3.46	1	12
-10.00	2	8,10
-15.12	2	4,5
-16.50	2	7,11
-16.92	2	3,6

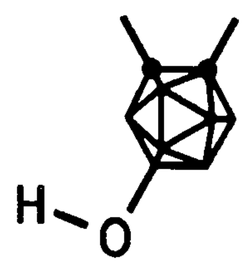


^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
49.06	a
37.01	b



9-hydroxy-1,2-dimethyl-1,2-dicarba-*closo*-dodecaborane

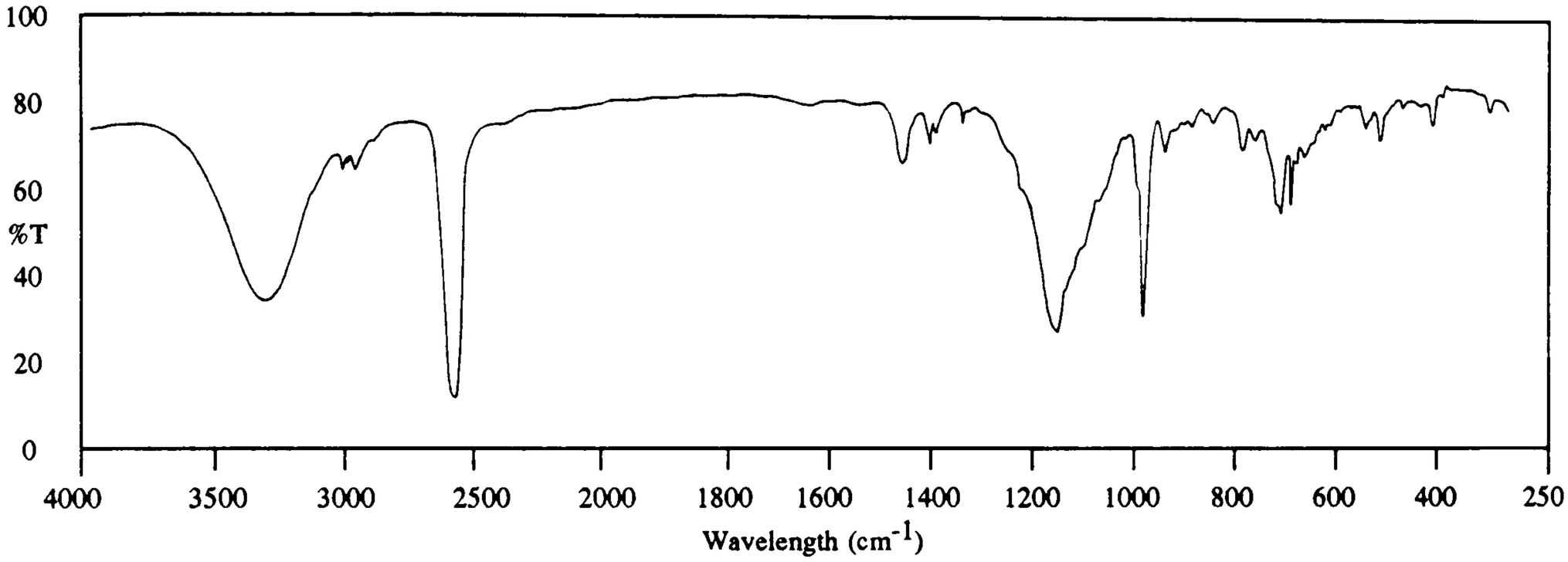


In a fume hood with an explosive screen, 1.72g (0.01 moles) 1,2-dimethyl-*ortho*-carborane was dissolved in 25ml of carbon tetrachloride with stirring. 11ml of fuming nitric acid was added very slowly to the solution giving off brown fumes and the solution was left to stir for 4 hours. It was poured into 100ml of water and the solid was filtered off, washed with carbon tetrachloride and dissolved in diethyl ether. The ether solution was dried over magnesium sulphate and filtered. Ether was vacuum-removed and the residue was recrystallized from a toluene : hexane mixture to give 0.43g (22.9%) of 9-hydroxy-1,2-dimethyl-*ortho*-carborane. The carbon tetrachloride solution was washed with water, sodium carbonate solution and then water again. After drying over anhydrous magnesium sulphate, carbon tetrachloride was driven off by rotary evaporator to leave a mixture of unreacted material and 9-nitrato-1,2-dimethyl-*ortho*-carborane. The mixture was dissolved in 15ml of absolute alcohol with stirring, 5g powdered tin metal and 8ml concentrated hydrochloric acid were added and refluxed for 3 hours. Ethanol was driven off with a rotary evaporator leaving a residue which was extracted with water and carbon tetrachloride. The undissolved material was filtered off and recrystallized from a toluene : hexane mixture to give a further 0.31g (16.5%, total 38.4%) of 9-hydroxy-1,2-dimethyl-*ortho*-carborane.

Melting point = 295-297°C (lit[39]. = 292-293°C)

Analysis Found: C,25.3; H,8.8. $C_{14}H_{20}B_{10}$ requires C,25.5; H,8.5.

Infrared (KBr disc; cm^{-1}) 3670-3038(s,br), 2992(w), 2974(w), 2943(w), 2582(s), 1450(w), 1398(w), 1386(w), 1337(w), 1273-1047(s,br), 1230(m), 1086(m), 994(s), 958(w), 941(w), 918(w), 903(w), 881(w), 867(w), 809(w), 782(w), 741(m), 732(m), 714(m), 702(w), 688(w), 672(w), 650(w), 570(w), 562(w), 501(w), 461(w), 442(w), 424(w), 334(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 190 corresponding to the species $^{12}C_2{}^{1}H_{12}{}^{11}B_{10}{}^{16}O$, accompanied by the usual carborane isotope distribution pattern between m/e 184 and 190. A group of peaks at m/e 167-173 were seen and identified as:

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

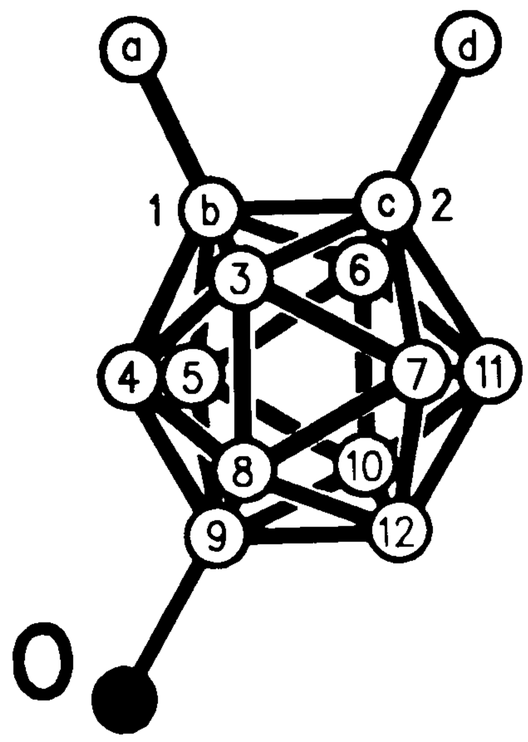
δ_{ppm}	intensity	type of peak	position of proton
3.20	1	broad singlet	O-H
2.16	3	singlet	methyl C(a)-H
2.09	3	singlet	methyl C(d)-H
4.0-0.9	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

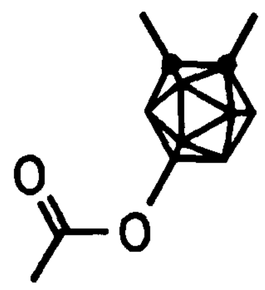
δ_{ppm}	intensity	position of boron
15.49	1	9
-5.24	1	12
-9.48	6	3,6,4,5,8,10
-10.99	2	7,11

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
68.13	b
55.80	c
23.66	a
20.60	d



9-acetoxy-1,2-dimethyl-1,2-dicarba-*closo*-dodecaborane

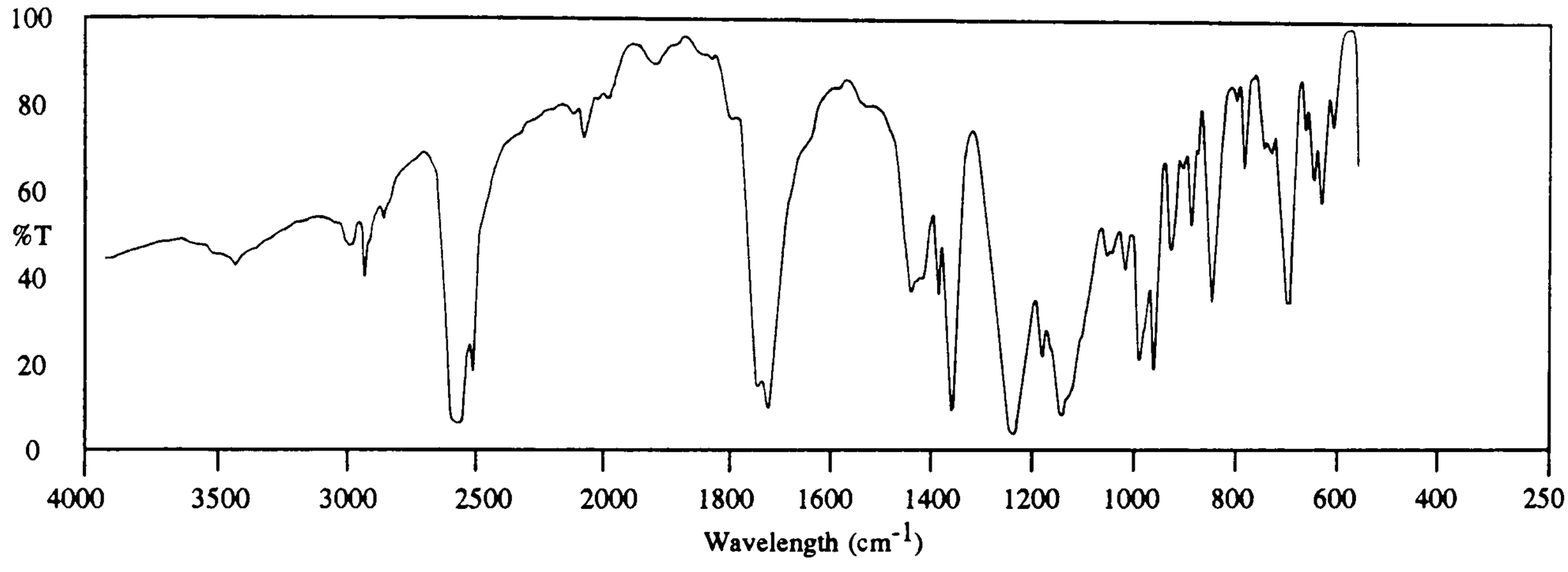


A solution of 0.19g (0.001 moles) of 9-hydroxy-1,2-dimethyl-*ortho*-carborane and 1ml of acetic anhydride was refluxed for 3 hours. When cooled, excess acetic anhydride was distilled off and the residue by gas chromatography showed two compounds of 96:4 area ratio at 21.8 and 24.2 minutes respectively. Attempts to separate these compounds by preparative gas-liquid chromatography were unsuccessful. The residue was recrystallized from hexane to give 0.16g (69.6%) of 9-acetoxy-1,2-dimethyl-*ortho*-carborane.

Melting point = 87-88°C

Analysis Found: C,30.6; H,7.6. $C_6H_{14}B_{10}O_2$ requires C,31.3; H,7.8.

Infrared (KBr disc; cm^{-1}) 2989(w), 2937(w), 2922(w), 2864(w), 2852(w), 2618(s), 2600(s), 2585(s), 2576(s), 2548(m), 2537(m), 2121(w), 1787(w), 1738(s), 1716(s), 1645(w), 1444(m), 1433(m), 1423(m), 1392(m), 1364(s), 1249(s), 1197(m), 1159(s), 1146(s), 1123(m), 1075(m), 1062(m), 1040(m), 1012(s), 1006(s), 987(s), 953(m), 932(w), 916(m), 905(w), 876(m), 831(w), 815(w), 778(w), 769(w), 763(w), 734(m), 729(m), 699(w), 682(w), 668(w), 647(w).



Mass spectrum (E.I.) A highest mass peak was observed at m/e 232 corresponding to the species $^{12}C_6{}^{1}H_{14}{}^{11}B_{10}{}^{16}O_2$, accompanied by the usual carborane isotope distribution pattern between m/e 226 and 232. A group of peaks at m/e 167-173 were seen and identified as:

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

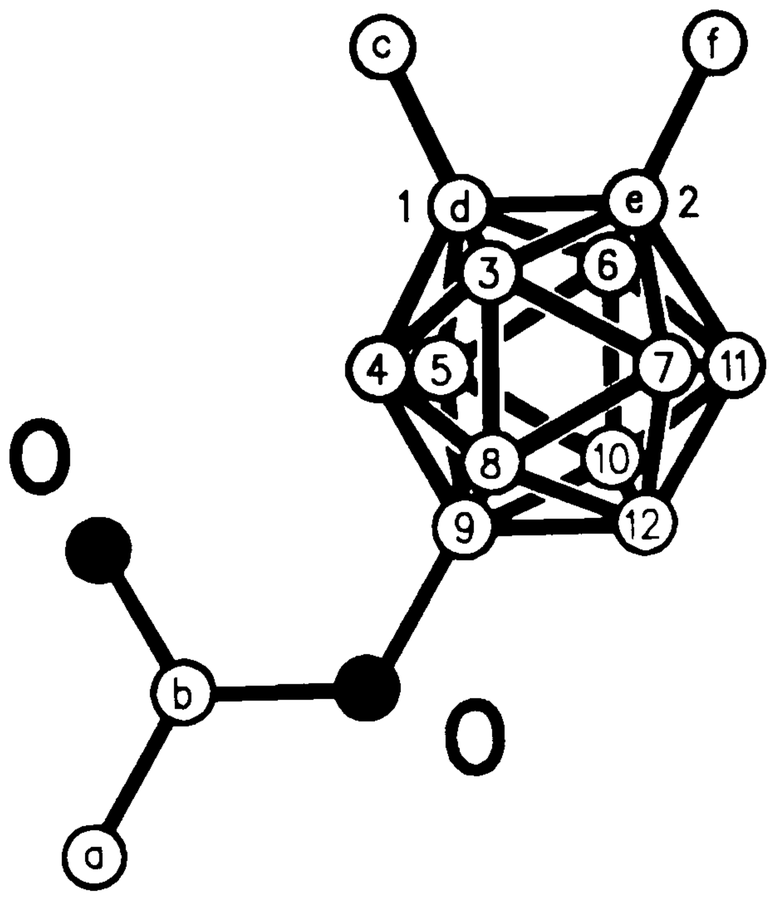
δ_{ppm}	intensity	type of peak	position of proton
2.06	3	singlet	methyl C(a)-H
2.04	3	singlet	methyl C(d)-H
2.01	3	singlet	methyl C(f)-H
4.0-0.8	9	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

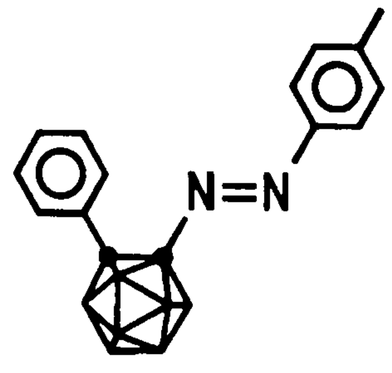
δ_{ppm}	intensity	position of boron
9.04	1	9
-6.27	1	12
-10.98	8	3,6,4,5,7,11,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
169.98	b
69.03	d
61.87	e
23.68	a
22.59	c
21.15	f



1-phenyl-2-(4-methylphenyl)azo-1,2-dicarba-*closo*-dodecaborane

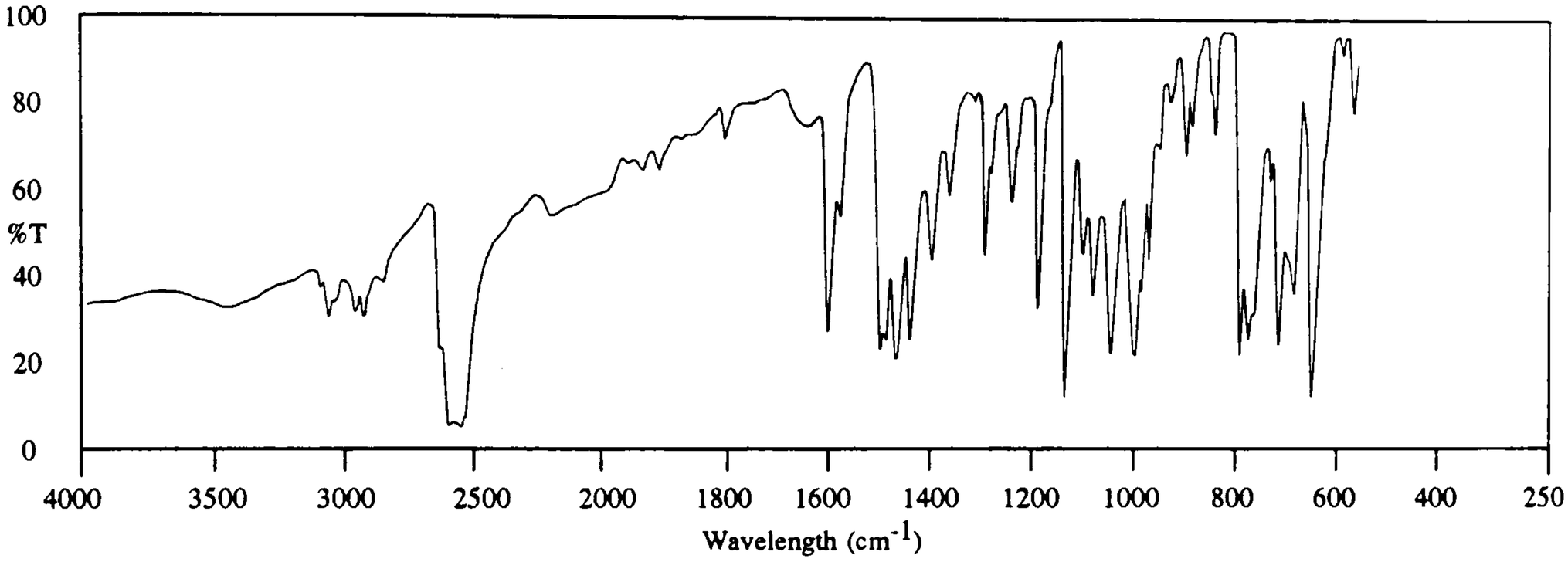


A stirred solution of 2.2g (0.01 moles) 1-phenyl-*ortho*-carborane in 30ml anhydrous diethyl ether was treated dropwise with 8ml (0.01 moles) of butyllithium in hexane (1.61M) under nitrogen at 0°C. After 20 minutes stirring the temperature of the cloudy solution was raised to 20°C for 10 minutes, then cooled to 0°C and 2.52g (0.0125 moles) of 4-methylbenzenediazonium tetrafluoroborate was added in small portions. A cloudy orange solution formed which was poured into 50ml water and the organic layer was washed with water, dried over anhydrous magnesium sulphate and filtered. The solvent was removed by rotary evaporator leaving a red residue which was recrystallized from hexane to give 2.77g (82.0%) yellow-orange crystals of 1-phenyl-2-(4-methylphenyl)azo-*ortho*-carborane.

Melting point = 90-91°C

Analysis Found: C,53.1; H,6.8; N,8.1. $C_{15}H_{22}B_{10}N_2$ requires C,53.3; H,6.5; N,8.3.

Infrared (KBr disc; cm^{-1}) 3084(w), 3052(w), 3033(w), 2957(w), 2922(w), 2867(w), 2852(w), 2642(m), 2603(s), 2566(s), 2545(s), 1797(w), 1600(s), 1578(m), 1500(s), 1489(s), 1472(s), 1446(s), 1408(m), 1376(w), 1328(w), 1308(m), 1297(w), 1258(w), 1249(w), 1208(m), 1190(w), 1157(s), 1136(m), 1106(m), 1071(s), 1026(s), 1013(m), 1002(m), 983(w), 961(w), 930(w), 919(w), 882(w), 878(w), 827(s), 810(s), 802(s), 769(w), 752(s), 736(m), 723(m), 688(s), 633(w), 611(w).



Mass spectrum (E.I.) The original compound seemed to dissociate rapidly on impact as no peak was present at m/e 338. A group of peaks between m/e 216 and 221 with the usual carborane isotope distribution pattern and a peak at m/e 91 were observed and identified respectively as:

^{1}H N.M.R. 250.134 MHz; solvent $CDCl_3$ referenced to 7.26ppm.

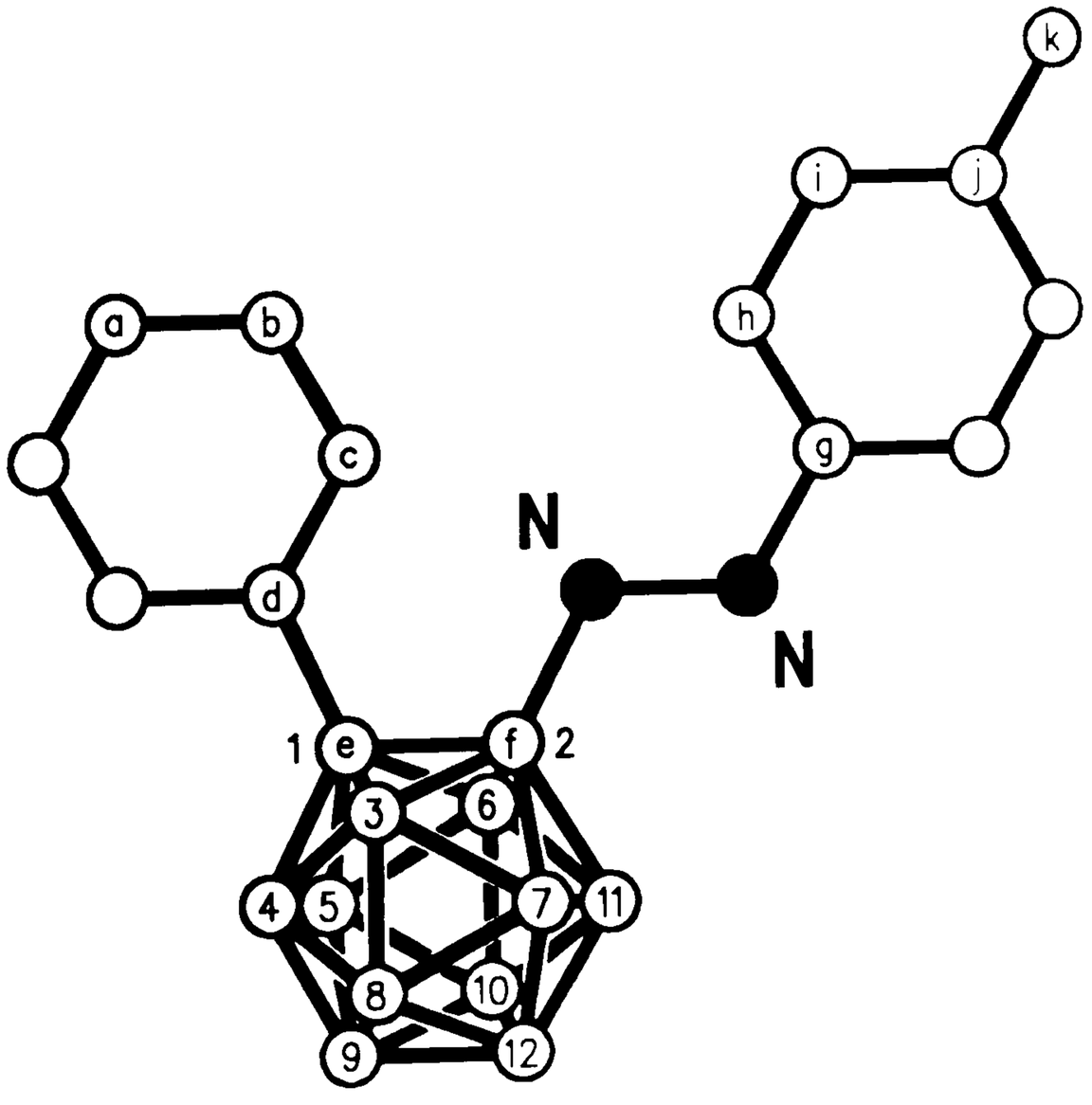
δ_{ppm}	intensity	type of peak	position of proton
7.72 7.69 7.19 7.16	4	doublet of doublets	aromatic C(h,i)-H
7.51-7.32	5	multiplet	aromatic C(a,b,c)-H
2.37	3	singlet	methyl C(k)-H
4.0-1.0	10	broad multiplet	carboranyl B-H

^{11}B N.M.R. {^{1}H broad band noise } 115.552 MHz; solvent $CDCl_3$, referenced externally to $BF_3.Et_2O$ at 0.00ppm.

δ_{ppm}	intensity	position of boron
-4.01	2	9,12
-10.71	8	3,6,4,5,7,11,8,10

^{13}C N.M.R. {^{1}H broad band noise } 62.896 MHz; solvent $CDCl_3$ referenced to 77.0ppm.

δ_{ppm}	position of carbon
149.11	g
144.40	j
131.09	b
130.44	d
130.18	a
129.82	c
128.22	i
123.45	h
98.83	e
81.80	f
21.56	k



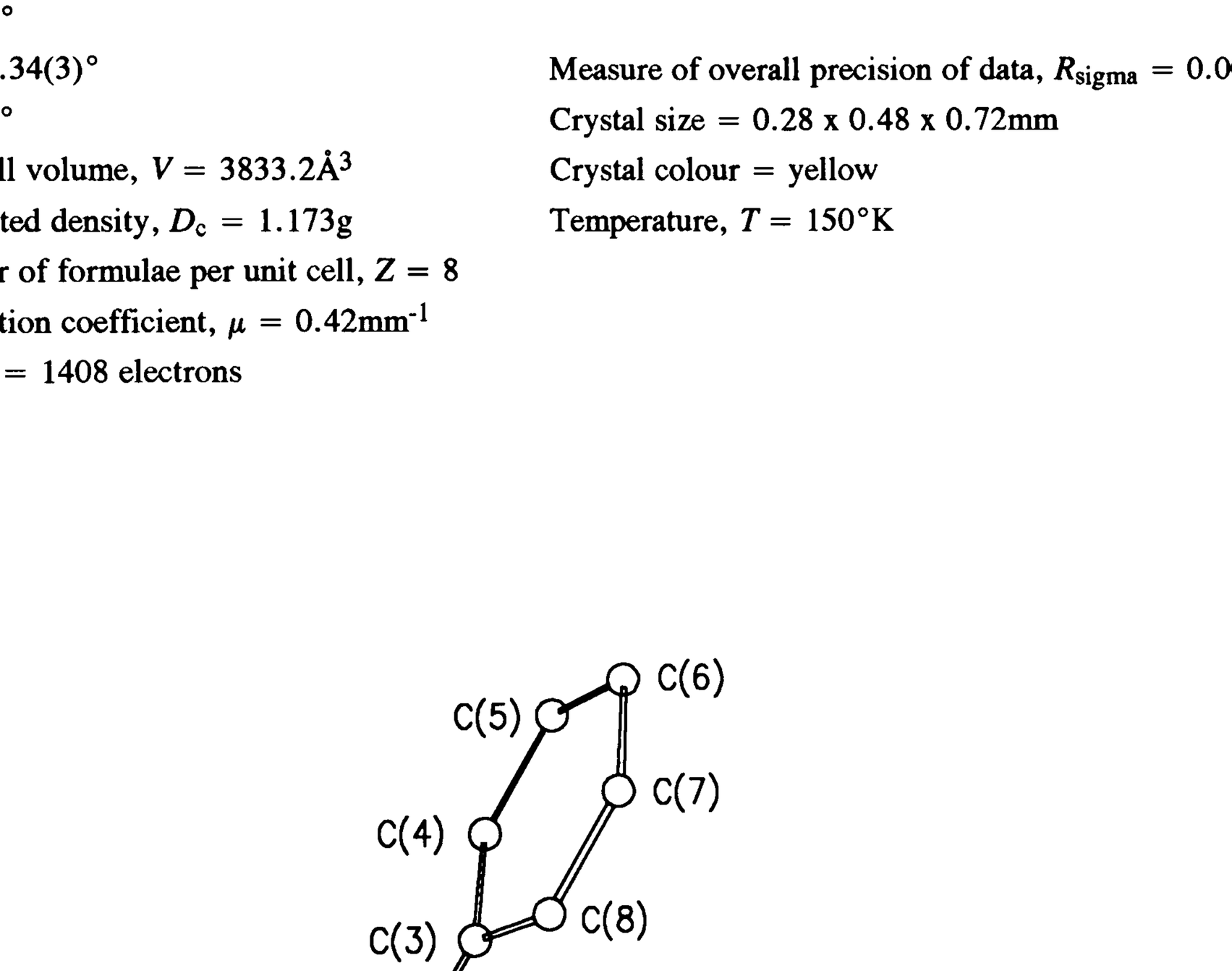
X-ray Analysis (W. Clegg, Newcastle University)

Crystallographic data, CuK_α radiation

Formula = $C_{15}H_{22}B_{10}N_2$
Formula weight, M_r = 338.5
System = monoclinic
Space Group = C2/c
a = 28.672(6)Å
b = 7.078(2)Å
c = 18.992(5)Å
α = 90°
β = 96.34(3)°
γ = 90°
Unit cell volume, V = 3833.2Å^3
Calculated density, D_c = 1.173g
Number of formulae per unit cell, Z = 8
Absorption coefficient, μ = 0.42mm^{-1}
F(000) = 1408 electrons

Number of unique reflections = 2964
Observed reflections, $F > 4\sigma_c(F)$ = 2878
$2\theta_{max}$ = 130°
Range, 2θ = 40 to 50°
Range, h = -33 to 33
Range, k = 0 to 8
Range, l = 0 to 22

Measure of overall precision of data, R_{sigma} = 0.006
Crystal size = 0.28 x 0.48 x 0.72mm
Crystal colour = yellow
Temperature, T = 150°K



Bond lengths (Å)

N(1)-N(2)	1.251(1)		N(1)-C(1)	1.450(2)
N(2)-C(9)	1.431(2)		C(1)-C(2)	1.690(2)
C(1)-B(1)	1.721(2)		C(1)-B(2)	1.699(2)
C(1)-B(3)	1.698(2)		C(1)-B(4)	1.709(2)
C(2)-C(3)	1.503(2)		C(2)-B(1)	1.740(2)
C(2)-B(4)	1.741(2)		C(2)-B(5)	1.711(2)
C(2)-B(6)	1.702(2)		C(3)-C(4)	1.400(2)
C(3)-C(8)	1.387(2)		C(4)-C(5)	1.381(2)
C(5)-C(6)	1.389(2)		C(6)-C(7)	1.376(2)
C(7)-C(8)	1.381(2)		C(9)-C(10)	1.398(2)
C(9)-C(14)	1.383(2)		C(10)-C(11)	1.373(2)
C(11)-C(12)	1.388(2)		C(12)-C(13)	1.392(2)
C(12)-C(15)	1.505(2)		C(13)-C(14)	1.378(2)
B(1)-H(1)	1.103(11)		B(1)-B(2)	1.768(2)
B(1)-B(6)	1.783(2)		B(1)-B(7)	1.762(3)
B(2)-H(2)	1.041(11)		B(2)-B(3)	1.783(2)
B(2)-B(7)	1.767(2)		B(2)-B(8)	1.780(2)
B(3)-H(3)	1.142(10)		B(3)-B(4)	1.779(3)
B(3)-B(8)	1.766(2)		B(3)-B(9)	1.765(2)
B(4)-H(4)	1.037(11)		B(4)-B(5)	1.770(2)
B(4)-B(9)	1.749(2)		B(5)-H(5)	1.054(12)
B(5)-B(6)	1.770(2)		B(5)-B(9)	1.778(2)
B(5)-B(10)	1.766(3)		B(6)-H(6)	1.114(9)
B(6)-B(7)	1.778(3)		B(6)-B(10)	1.772(2)
B(7)-H(7)	1.035(13)		B(7)-B(8)	1.786(2)
B(7)-B(10)	1.779(2)		B(8)-H(8)	1.051(13)
B(8)-B(9)	1.783(2)		B(8)-B(10)	1.780(2)
B(9)-H(9)	1.006(11)		B(9)-B(10)	1.783(2)
B(10)-H(10)	1.069(11)			

Bond angles (°)

N(2)-N(1)-C(1)	112.9(1)		N(1)-N(2)-C(9)	112.8(1)
N(1)-C(1)-C(2)	111.3(1)		N(1)-C(1)-B(1)	116.2(1)
C(2)-C(1)-B(1)	61.3(1)		N(1)-C(1)-B(2)	126.5(1)
C(2)-C(1)-B(2)	111.6(1)		B(1)-C(1)-B(2)	62.2(1)
N(1)-C(1)-B(3)	124.0(1)		C(2)-C(1)-B(3)	112.3(1)
B(1)-C(1)-B(3)	114.8(1)		B(2)-C(1)-B(3)	63.3(1)
N(1)-C(1)-B(4)	112.8(1)		C(2)-C(1)-B(4)	61.6(1)
B(1)-C(1)-B(4)	114.2(1)		B(2)-C(1)-B(4)	115.0(1)
B(3)-C(1)-B(4)	63.0(1)		C(1)-C(2)-C(3)	118.7(1)
C(1)-C(2)-B(1)	60.2(1)		C(3)-C(2)-B(1)	116.3(1)
C(1)-C(2)-B(4)	59.7(1)		C(3)-C(2)-B(4)	119.0(1)
B(1)-C(2)-B(4)	111.7(1)		C(1)-C(2)-B(5)	108.6(1)
C(3)-C(2)-B(5)	123.3(1)		B(1)-C(2)-B(5)	113.2(1)
B(4)-C(2)-B(5)	61.7(1)		C(1)-C(2)-B(6)	109.2(1)
C(3)-C(2)-B(6)	121.7(1)		B(1)-C(2)-B(6)	62.4(1)
B(4)-C(2)-B(6)	112.7(1)		B(5)-C(2)-B(6)	62.5(1)
C(2)-C(3)-C(4)	119.5(1)		C(2)-C(3)-C(8)	122.2(1)
C(4)-C(3)-C(8)	118.3(1)		C(3)-C(4)-C(5)	120.8(1)
C(4)-C(5)-C(6)	120.0(1)		C(5)-C(6)-C(7)	119.5(1)
C(6)-C(7)-C(8)	120.7(1)		C(3)-C(8)-C(7)	120.7(1)
N(2)-C(9)-C(10)	123.9(1)		N(2)-C(9)-C(14)	116.3(1)
C(10)-C(9)-C(14)	119.8(1)		C(9)-C(10)-C(11)	119.3(1)
C(10)-C(11)-C(12)	121.6(1)		C(11)-C(12)-C(13)	118.3(1)
C(11)-C(12)-C(15)	120.9(1)		C(13)-C(12)-C(15)	120.8(1)
C(12)-C(13)-C(14)	120.8(1)		C(9)-C(14)-C(13)	120.1(1)
C(1)-B(1)-C(2)	58.4(1)		C(1)-B(1)-H(1)	116.6(6)
C(2)-B(1)-H(1)	117.0(6)		C(1)-B(1)-B(2)	58.3(1)
C(2)-B(1)-B(2)	106.1(1)		H(1)-B(1)-B(2)	122.8(6)
C(1)-B(1)-B(6)	104.2(1)		C(2)-B(1)-B(6)	57.8(1)
H(1)-B(1)-B(6)	125.9(6)		B(2)-B(1)-B(6)	108.1(1)
C(1)-B(1)-B(7)	104.2(1)		C(2)-B(1)-B(7)	105.0(1)
H(1)-B(1)-B(7)	132.2(6)		B(2)-B(1)-B(7)	60.1(1)
B(6)-B(1)-B(7)	60.2(1)		C(1)-B(2)-B(1)	59.5(1)
C(1)-B(2)-H(2)	118.5(7)		B(1)-B(2)-B(2)	117.7(6)
C(1)-B(2)-B(3)	58.3(1)		B(1)-B(2)-B(3)	108.4(1)
H(2)-B(2)-B(3)	120.7(6)		C(1)-B(2)-B(7)	104.8(1)
B(1)-B(2)-B(7)	59.8(1)		H(2)-B(2)-B(7)	126.5(6)
B(3)-B(2)-B(7)	107.9(1)		C(1)-B(2)-B(8)	104.2(1)
B(1)-B(2)-B(8)	108.4(1)		H(2)-B(2)-B(8)	128.2(7)
B(3)-B(2)-B(8)	59.5(1)		B(7)-B(2)-B(8)	60.5(1)
C(1)-B(3)-B(2)	58.4(1)		C(1)-B(3)-H(3)	120.2(6)
B(2)-B(3)-H(3)	123.7(5)		C(1)-B(3)-B(4)	58.8(1)
B(2)-B(3)-B(4)	107.6(1)		H(3)-B(3)-B(4)	116.7(6)
C(1)-B(3)-B(8)	104.8(1)		B(2)-B(3)-B(8)	60.2(1)
H(3)-B(3)-B(8)	128.1(6)		B(4)-B(3)-B(8)	107.7(1)
C(1)-B(3)-B(9)	104.5(1)		B(2)-B(3)-B(9)	108.4(1)
H(3)-B(3)-B(9)	123.3(5)		B(4)-B(3)-B(9)	59.1(1)
B(8)-B(3)-B(9)	60.7(1)		C(1)-B(4)-C(2)	58.7(1)
C(1)-B(4)-B(3)	58.2(1)		C(2)-B(4)-B(3)	106.1(1)
C(1)-B(4)-H(4)	118.4(6)		C(2)-B(4)-H(4)	115.2(6)
B(3)-B(4)-H(4)	126.1(6)		C(1)-B(4)-B(5)	105.1(1)
C(2)-B(4)-B(5)	58.3(1)		B(3)-B(4)-B(5)	108.4(1)
H(4)-B(4)-B(5)	122.1(6)		C(1)-B(4)-B(9)	104.7(1)

C(2)-B(4)-B(9)	105.8(1)	B(3)-B(4)-B(9)	60.0(1)
H(4)-B(4)-B(9)	131.2(6)	B(5)-B(4)-B(9)	60.7(1)
C(2)-B(5)-B(4)	60.0(1)	C(2)-B(5)-H(5)	113.6(7)
B(4)-B(5)-H(5)	116.5(6)	C(2)-B(5)-B(6)	58.5(1)
B(4)-B(5)-B(6)	108.1(1)	H(5)-B(5)-B(6)	119.5(6)
C(2)-B(5)-B(9)	105.9(1)	B(4)-B(5)-B(9)	59.1(1)
H(5)-B(5)-B(9)	128.8(6)	B(6)-B(5)-B(9)	108.4(1)
C(2)-B(5)-B(10)	105.5(1)	B(4)-B(5)-B(10)	107.5(1)
H(5)-B(5)-B(10)	131.4(7)	B(6)-B(5)-B(10)	60.1(1)
B(9)-B(5)-B(10)	60.4(1)	C(2)-B(6)-B(1)	59.8(1)
C(2)-B(6)-B(5)	59.0(1)	B(1)-B(6)-B(5)	108.3(1)
C(2)-B(6)-H(6)	113.1(7)	B(1)-B(6)-H(6)	115.4(6)
B(5)-B(6)-H(6)	120.3(6)	C(2)-B(6)-B(7)	105.9(1)
B(1)-B(6)-B(7)	59.3(1)	B(5)-B(6)-B(7)	108.0(1)
H(6)-B(6)-B(7)	128.6(6)	C(2)-B(6)-B(10)	105.6(1)
B(1)-B(6)-B(10)	107.6(1)	B(5)-B(6)-B(10)	59.8(1)
H(6)-B(6)-B(10)	132.3(6)	B(7)-B(6)-B(10)	60.1(1)
B(1)-B(7)-B(2)	60.1(1)	B(1)-B(7)-B(6)	60.5(1)
B(2)-B(7)-B(6)	108.4(1)	B(1)-B(7)-H(7)	121.3(8)
B(2)-B(7)-H(7)	120.9(7)	B(6)-B(7)-H(7)	122.2(7)
B(1)-B(7)-B(8)	108.4(1)	B(2)-B(7)-B(8)	60.1(1)
B(6)-B(7)-B(8)	108.0(1)	H(7)-B(7)-B(8)	121.3(8)
B(1)-B(7)-B(10)	108.2(1)	B(2)-B(7)-B(10)	108.0(1)
B(6)-B(7)-B(10)	59.8(1)	H(7)-B(7)-B(10)	122.3(7)
B(8)-B(7)-B(10)	59.9(1)	B(2)-B(8)-B(3)	60.4(1)
B(2)-B(8)-B(7)	59.4(1)	B(3)-B(8)-B(7)	107.8(1)
B(2)-B(8)-H(8)	122.6(6)	B(3)-B(8)-H(8)	120.6(6)
B(7)-B(8)-H(8)	123.5(6)	B(2)-B(8)-B(9)	107.7(1)
B(3)-B(8)-B(9)	59.6(1)	B(7)-B(8)-B(9)	107.7(1)
H(8)-B(8)-B(9)	120.6(6)	B(2)-B(8)-B(10)	107.4(1)
B(3)-B(8)-B(10)	107.8(1)	B(7)-B(8)-B(10)	59.8(1)
H(8)-B(8)-B(10)	122.2(6)	B(9)-B(8)-B(10)	60.1(1)
B(3)-B(9)-B(4)	60.8(1)	B(3)-B(9)-B(5)	108.7(1)
B(4)-B(9)-B(5)	60.3(1)	B(3)-B(9)-B(8)	59.7(1)
B(4)-B(9)-B(8)	108.3(1)	B(5)-B(9)-B(8)	107.8(1)
B(3)-B(9)-H(9)	117.9(6)	B(4)-B(9)-H(9)	116.9(8)
B(5)-B(9)-H(9)	122.3(7)	B(8)-B(9)-H(9)	123.9(8)
B(3)-B(9)-B(10)	107.7(1)	B(4)-B(9)-B(10)	107.7(1)
B(5)-B(9)-B(10)	59.5(1)	B(8)-B(9)-B(10)	59.9(1)
H(9)-B(9)-B(10)	127.1(7)	B(5)-B(10)-B(6)	60.1(1)
B(5)-B(10)-B(7)	108.2(1)	B(6)-B(10)-B(7)	60.1(1)
B(5)-B(10)-B(8)	108.5(1)	B(6)-B(10)-B(8)	108.5(1)
B(7)-B(10)-B(8)	60.2(1)	B(5)-B(10)-B(9)	60.1(1)
B(6)-B(10)-B(9)	108.1(1)	B(7)-B(10)-B(9)	108.0(1)
B(8)-B(10)-B(9)	60.1(1)	B(5)-B(10)-H(10)	119.2(7)
B(6)-B(10)-H(10)	123.9(6)	B(7)-B(10)-H(10)	125.4(6)
B(8)-B(10)-H(10)	121.1(7)	B(9)-B(10)-H(10)	118.0(6)

APPENDIX A

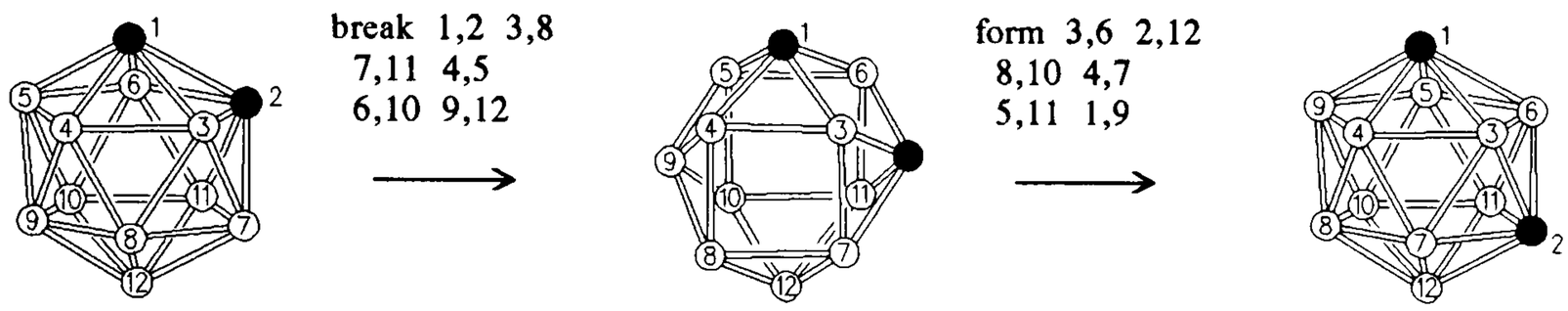
MECHANISMS OF REARRANGEMENTS

POSTULATED MECHANISMS

The mechanism of thermal icosahedral carborane isomerization has been the subject of many theories. In view of renewed interest and lack of clarity in some papers the considered mechanisms are investigated in detail with diagrams.

The first mechanism theory was postulated using a cuboctahedral intermediate[1]. However it was found that this mechanism could not explain the formation of *para* isomer[2].

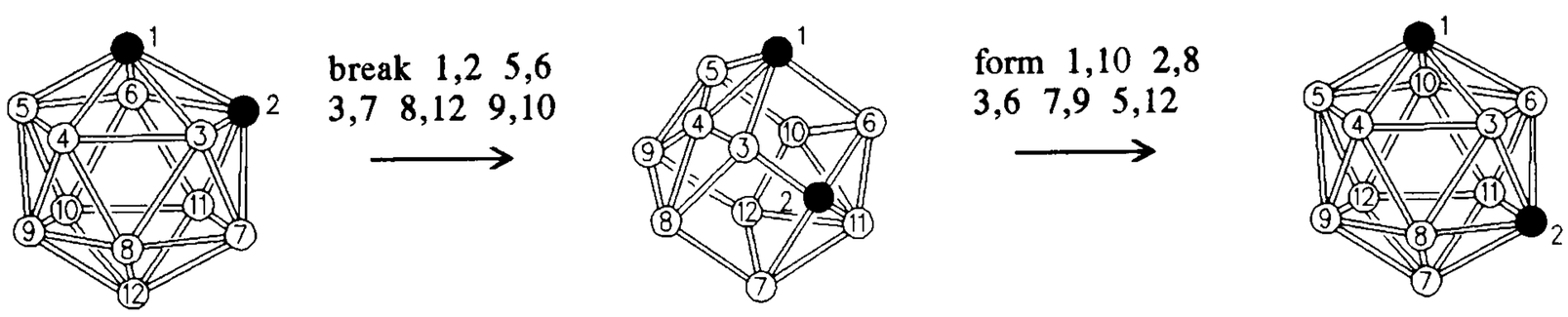
Concerted via cuboctahedron intermediate



CC1 **CC2** **CC3**

The pentagonal bipyramid mechanism[3] was used to explain the presence of *para* isomer. Other postulated routes used a modified version of the cuboctahedral intermediate with rotation at one of the faces, triangular[4] or square, which can lead to *para* isomer formation by a simple 120° rotation of a triangular face[5].

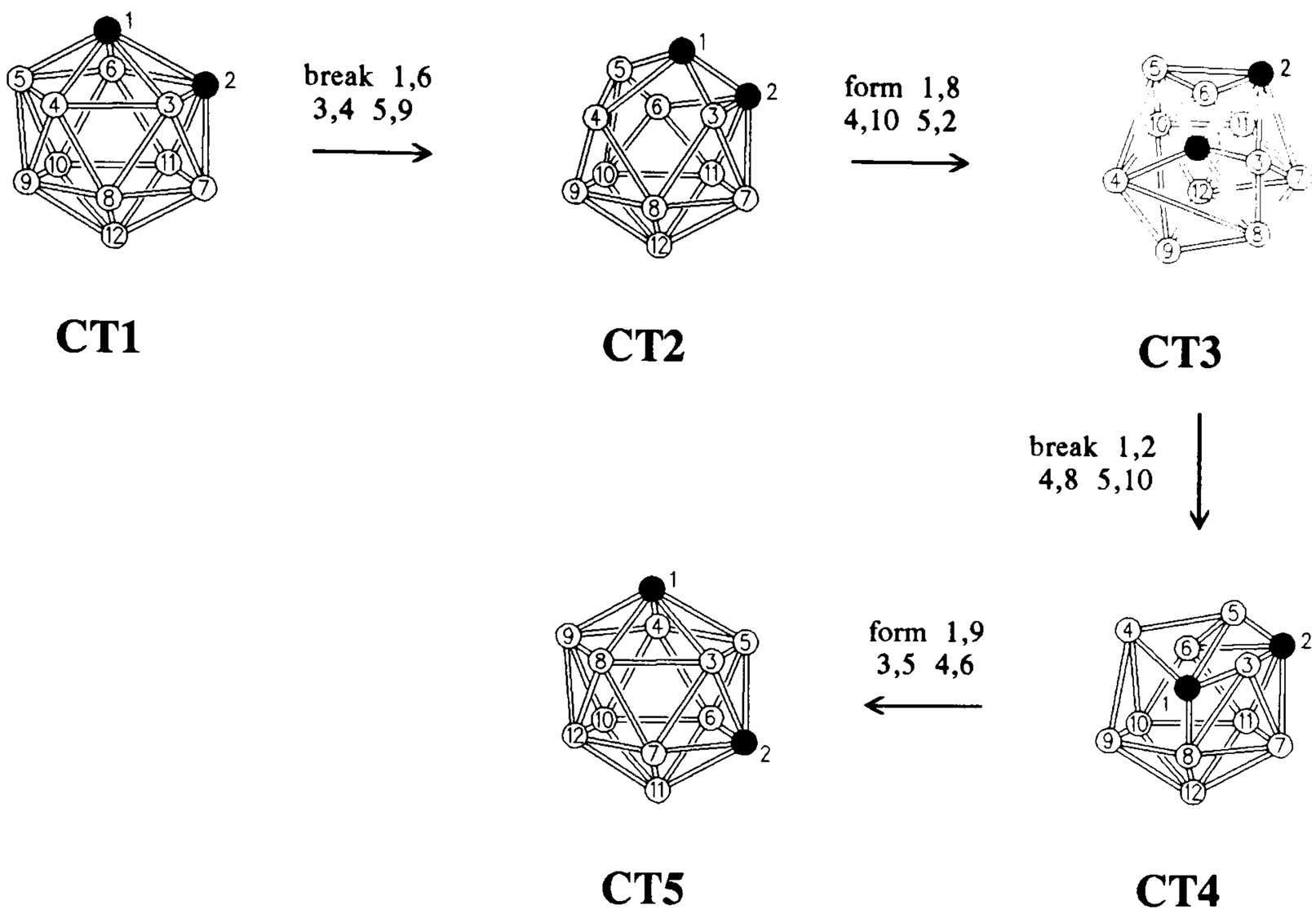
Concerted pentagonal bipyramid rotation



CP1 **CP2** **CP3**

1. Hoffmann R. Lipscomb W.N. *Inorg. Chem.* 1963 **2** 231-232
2. Lipscomb W.N. *Science* 1966 **153** 373-378
3. Grafstein D. Dvorak J. *Inorg. Chem.* 1963 **2** 1128-1133
4. Kaesz H.D. Bau R. Beall H.A. Lipscomb W.N. *J. Am. Chem. Soc.* 1967 **89** 4218-4220
5. Muetterties E.L. Knoth W.L. "Polyhedral Boranes" Marcel Dekker Inc., New York 1968 p70

Concerted 120° triangular face rotation



Labelling a boron atom of the carborane with a substituent like a halogen for thermal isomerization was used to determine the most likely mechanism. The isomers from thermal rearrangement of a halogenated carborane isomer were identified and compared with those expected from considered mechanisms. The results correlated well with selective triangle rotation in the cuboctahedral intermediate compared with other mechanisms[1,6,7,8].

But all the mechanisms mentioned did not explain the ratio of isomers formed by thermal rearrangement of 12-chloro-1,2-phosphacarborane[9]. A different mechanism[65] via the *nido*-intermediate gave better predictions. Possible migration[10,11] and the electronic effect[5,6] of the halogen atom were used as possible reasons for unexplained isomers.

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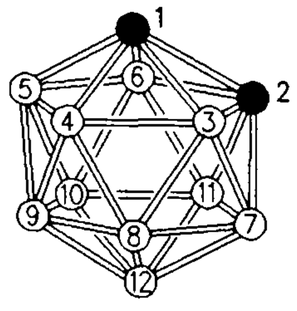
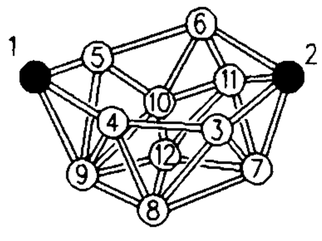
6. Stanko V.I. Klimova A.I. Gol'yapin Yu.V. *J. Gen. Chem. U.S.S.R.* 1969 **39** 1765-1767
7. Hart H.V. Lipscomb W.N. *J. Am. Chem. Soc.* 1969 **91** 771-772
8. Hart H.V. Lipscomb W.N. *Inorg. Chem.* 1973 **12** 2644-2649
9. Wong H.S. Lipscomb W.N. *Inorg. Chem.* 1975 **14** 1350-1357
10. Stanko V.I. Klimova A.I. *J. Gen. Chem. U.S.S.R.* 1969 **39** 1765-1767
11. Zakharkin L.I. Kalinin V.N. *Bull. Acad. Sci. U.S.S.R., Chem. Div.* 1969 **3** 542-545



N1

break 1,2 1,3
1,6 4,5

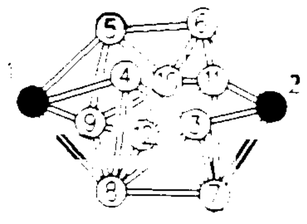
form 1,9



N2

break 4,9

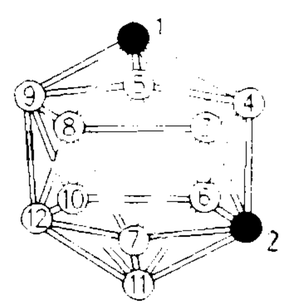
form 1,8



N3

break 4,8
form 4,5 4,6
4,2 1,3

Concerted via *nido* intermediate



N4

Cohesive energy calculations pointed to a stepwise mechanism rather than concerted[12]. A stepwise mechanism theory uses a cap - edge-bridged - cap interconversion. This mechanism was considered unfavourable due to the formation of a tetrahedral cap which would require a decrease in the number of skeletal electron pairs[13].

Orbital geometry calculations also favour a stepwise as opposed to a concerted mechanism[13]. No low-energy rearrangement pathway was correctly predicted for icosahedral carboranes as a mirror plane during some rearrangement steps is conserved resulting in 'forbidden' orbital crossings according to calculations derived from tensor surface harmonic (TSH) theory. Stepwise versions of the simple cuboctahedral and pentagonal bipyramid rotation mechanisms were proposed. The former, despite more steps, is preferred to the latter as the intermediates are more spherical geometrically in the former mechanism.

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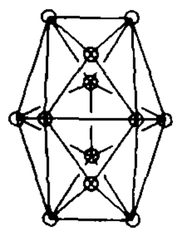
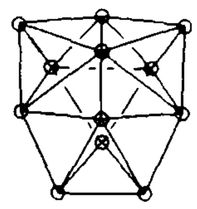
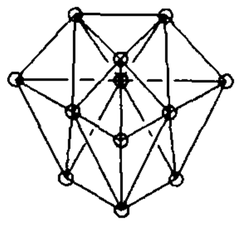
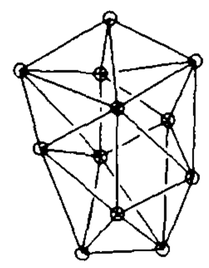
12. Johnson B.F.G. *J. Chem. Soc. Chem. Comm.* 1986 27-30
13. Wales D.J. Mingos D.M.P. Zhenyang L. *Inorg. Chem.* 1989 **28** 2754-2764

Types of 12-vertex polyhedron intermediates possibly involved in stepwise rearrangements[13].

A 

B 

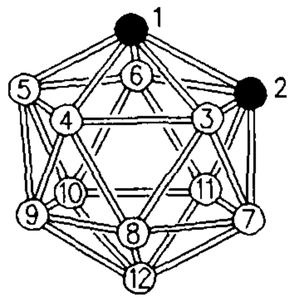
C 

D 

Type A is present in all stepwise mechanisms

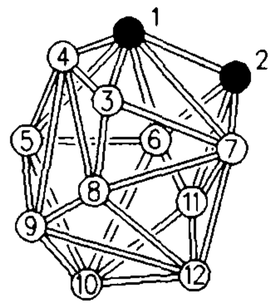
Type D is very distorted from a spherical geometry

Stepwise via edge bridge

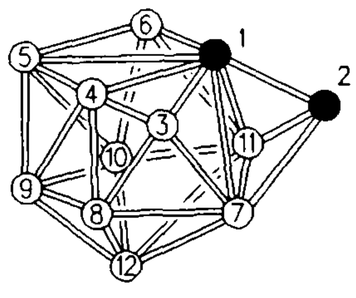


SE1

break 2,3
form 1,7

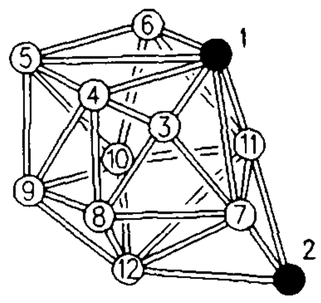


SE2



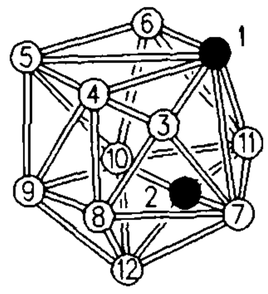
SE3

break 1,2
form 2,12



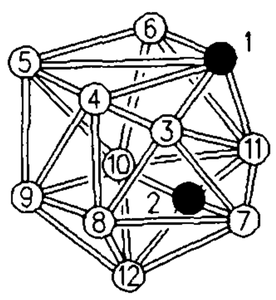
SE4

break 11,12
form 2,10



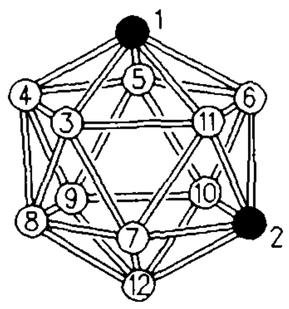
SE5

break 1,7
form 3,11



SE6

break 10,11
form 2,10



SE7

SE2 = polyhedron A

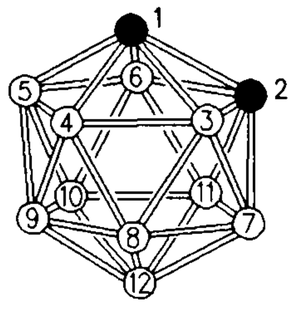
SE3 = 11-vertex polyhedron with tetrahedral cap

SE4 = 11-vertex polyhedron with tetrahedral cap

SE5 = polyhedron B

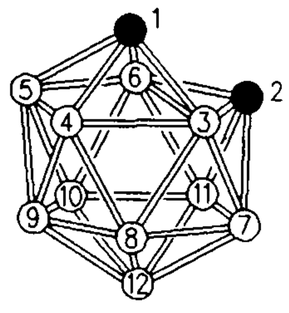
SE6 = polyhedron A

Stepwise via cuboctahedron intermediate



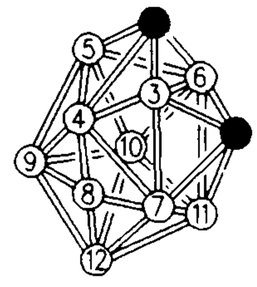
SC1

break 1,2
form 3,6



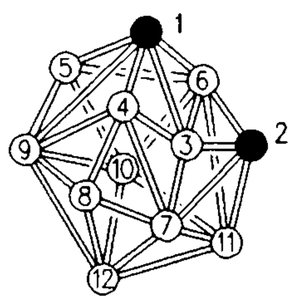
SC2

break 3,8
form 4,7



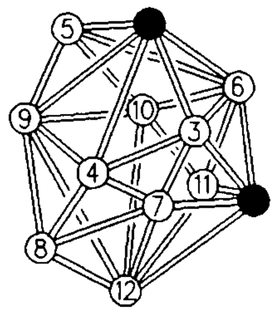
SC3

break 4,5
form 1,9



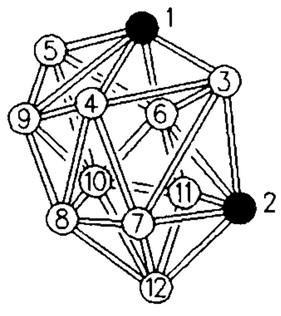
SC4

break 7,11
form 2,12



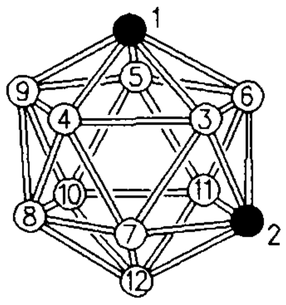
SC5

break 9,12
form 8,10



SC6

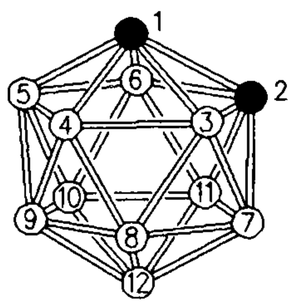
break 6,10
form 5,11



SC7

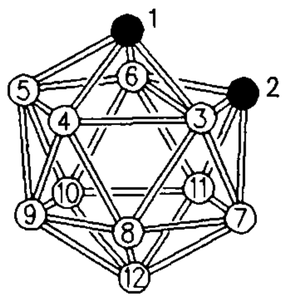
SC2 = polyhedron A
SC3 = polyhedron B
SC4 = polyhedron C
SC5 = polyhedron B
SC6 = polyhedron A

SP2 = polyhedron A
SP3 = polyhedron D
SP4 = polyhedron D
SP5 = polyhedron A



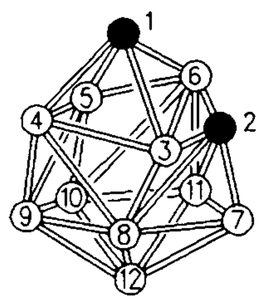
SP1

break 1,2
form 3,6



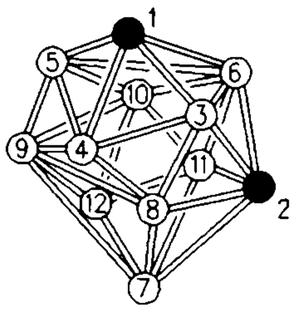
SP2

break 3,7
form 2,8



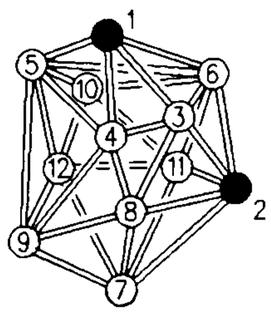
SP3

break 8,12
form 7,9



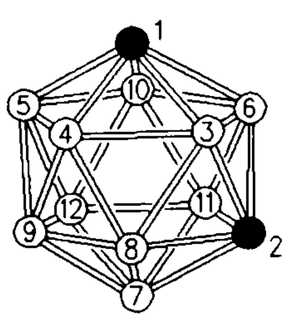
SP4

break 9,10
form 5,12



SP5

break 5,6
form 1,10

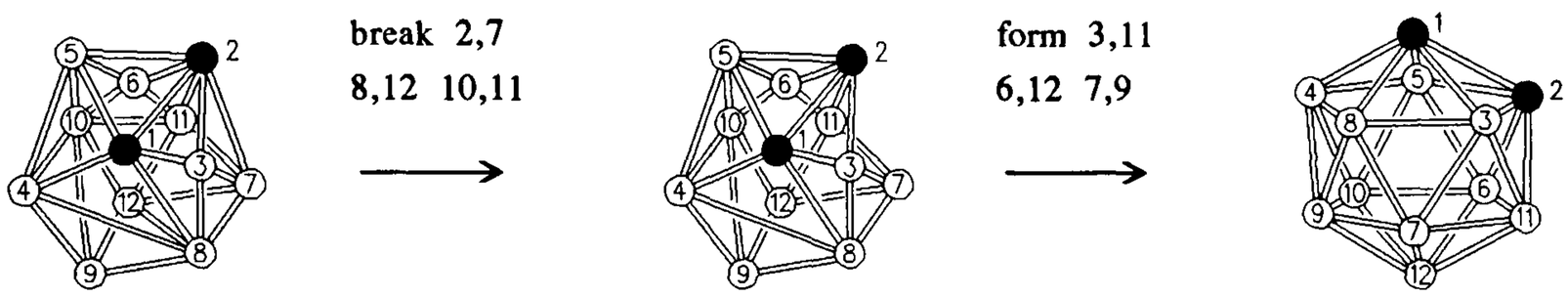


SP6

Stepwise pentagonal bipyramid rotation

Recently there have been two further approaches to tackling the thermal rearrangement mechanism. One approach used a carbon-boron bridged carborane and proposed the extended triangular rotation (ETR) mechanism which is a modification of the 120° triangular mechanism[14]. The triangle directly opposite the triangle already rotated by 60° in the **CT3** intermediate is rotated anti-clockwise or clockwise by 60° to produce two new configurations, one of which gives the same product as expected from a simple cubooctahedral mechanism. This route is less favourable than the simple 120° triangle mechanism.

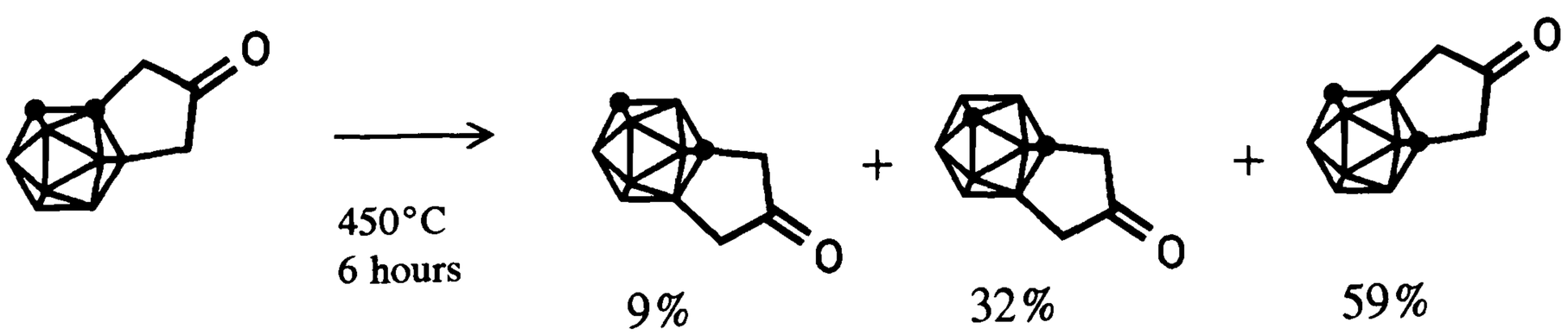
Extended triangular face rotation



CT3 **CT6** **CT7**

CT3 could also form another configuration by breaking 2,11 7,8 and 10,12 bonds and forming 3,12 6,7 and 9,11 bonds.

The ETR mechanism does correlate well with all experimental data on carborane thermal rearrangement products including the carbon-boron bridged carborane (diagram below) and 12-chloro-1,2-phosphacarborane.



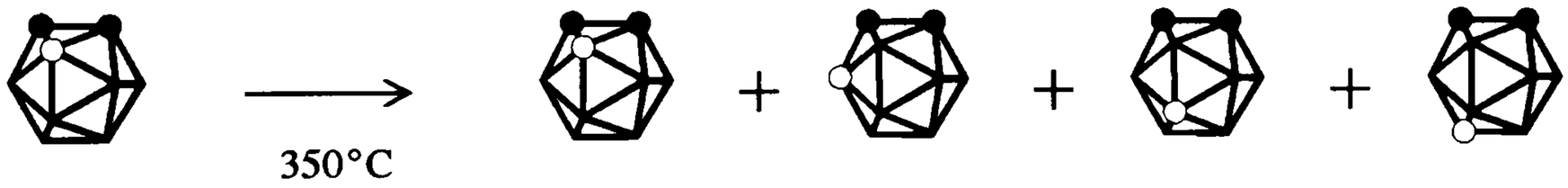
14. Wu S-h. Jones M.Jr. *J. Am. Chem. Soc.* 1989 **11** 5373-5384

The other recent approach used the "ideal" labelled carboranes, two ^{10}B enriched *ortho* and *meta* isomers, and a ^{10}B-F carborane[15]. The latter compound was used to observe possible intramolecular migration of the halogen atom. The bond did not cleave in products from heating the compound at 395°C for several hours confirming no halogen migration.

The ^{10}B *ortho*-carborane isomer formed several ^{10}B *ortho*-carborane isomers at 350°C (diagram below) indicating that transposition of the boron positions occurs faster than that of the carbons from *ortho* to *meta*. The ^{10}B *meta*-carborane isomer showed no rearrangement of the ^{10}B atom or to *ortho*-carborane at 470°C.

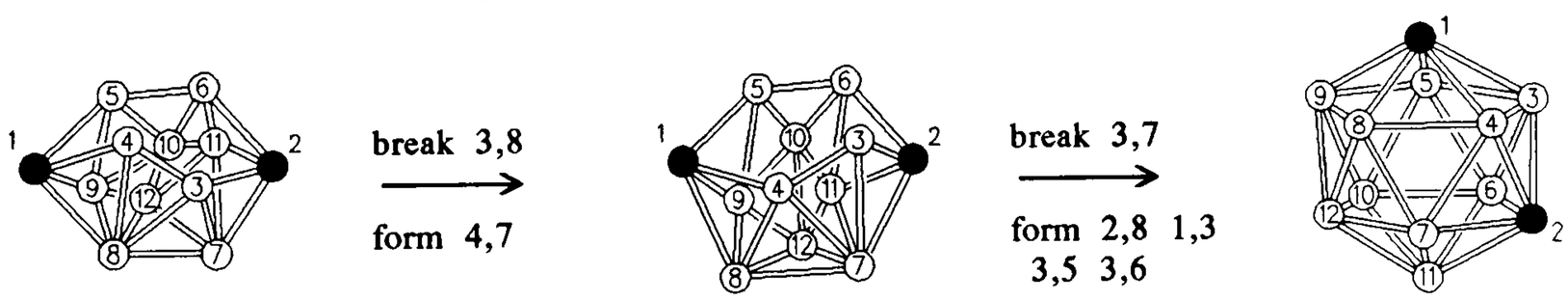
In the ^{10}B atom rearrangement of 3-^{10}B *ortho*-carborane at 350°C, the distributions of isomers were observed with time and compared with all postulated mechanisms apart from 120° triangular rotation. Rearrangements involving a *nido* intermediate and preferred B-B bond openings were favoured and all isomers are possible by using diamond-square-diamond processes on the *nido* intermediate. This mechanism was preferred partly as the *nido* intermediate is present in 13-atom cobalt complexes containing carborane ligands which rearrange readily.

circle denotes ^{10}B



3-isomer 3-isomer 4-isomer 8-isomer 9-isomer

Extension via *nido* intermediate



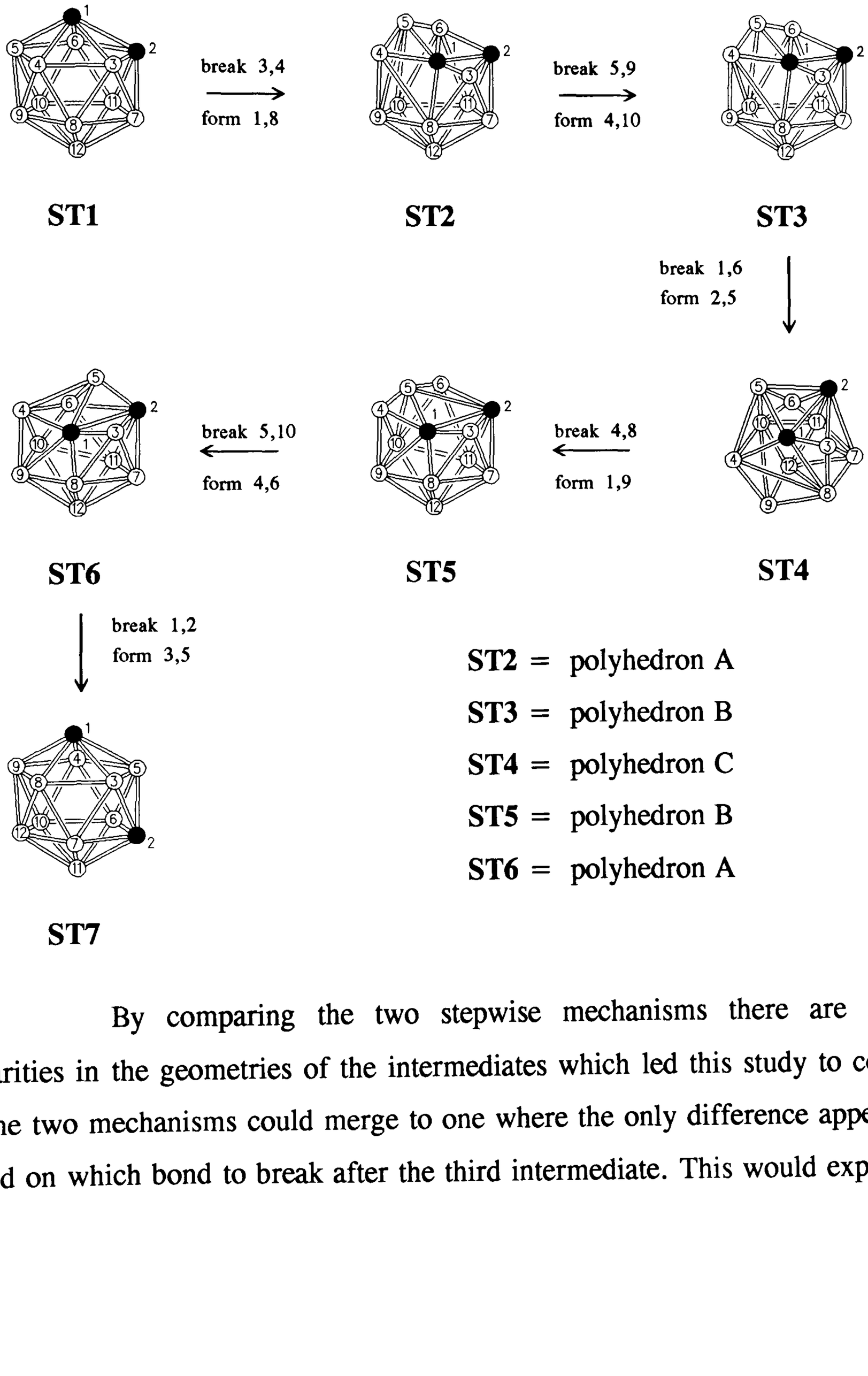
N3 **N5** **N6**

N5 could form another intermediate by breaking 2,7 and forming 3,11 bonds so another configuration could be produced. The modified mechanism could give any isomers via diamond-square-diamond processes in the *nido* intermediate.

15. Edvenson G.M. Gaines D.F. *Inorg. Chem.* 1990 **29** 1210-1216

It is concluded that there is no universally accepted mechanism for thermal rearrangement of icosahedral carboranes. However all mechanisms involve diamond-square-diamond processes and if stepwise rearrangement steps with geometrically acceptable intermediates are preferred then this narrows down to the stepwise version of the simple cuboctahedral intermediate and a new stepwise version of the 120° triangular rotation.

Stepwise 120° triangular face rotation



ST2 = polyhedron A

ST3 = polyhedron B

ST4 = polyhedron C

ST5 = polyhedron B

ST6 = polyhedron A

By comparing the two stepwise mechanisms there are striking similarities in the geometries of the intermediates which led this study to conclude that the two mechanisms could merge to one where the only difference appeared to depend on which bond to break after the third intermediate. This would explain the

similarity of the ETR and the modified cuboctahedral mechanism in the theoretical yields.

This study favours the stepwise version of the ETR mechanism for thermal rearrangement of carboranes and a different mechanism for the isomerization via cobalt complexes which could in fact be the modified mechanism via the *nido* intermediate.

APPENDIX B

COLLOQUIA, LECTURES AND SEMINARS

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing all research colloquia, research seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student.

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS

Alder Dr. B.J. (Lawrence Livermore Labs., California) "Hydrogen in all its Glory"	15th January 1991
Aveyard Dr. R. (University of Hull) "Surfactants at your Surface"	15th March 1989
Aylett Prof. B.J. (Queen Mary College, London) "Silicon-Based Chips:- The Chemist's Contribution"	16th February 1989
Badyal Dr. J.P.S. (Durham University) "Breakthrough in Heterogenous Catalysis"	1st November 1989
Baldwin Prof. J.E. (Oxford University) "Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis"	9th February 1989
Baldwin and Walker Drs. R.R. and R.W. (Hull University) "Combustion: Some Burning Problems"	24th November 1988
Becher Dr.J. (Odense University) "Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks"	13th November 1989
Bell Prof. T. (SUNY, Stoney Brook, U.S.A.) "Functional Molecular Architecture and Molecular Recognition"	14th November 1990
Bercaw Prof. J.E. (California Institute of Technology) "Synthetic and Mechanistic Approaches to Ziegler-Natta Polymerization of Olefins"	10th November 1989
Bleasdale Dr. C. (Newcastle University) "The Mode of Action of some Anti-tumour Agents"	21st February 1990
Bochmann Dr. M. (University of East Anglia) "Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls"	24th October 1990
Bowman Prof. J.M. (Emory University) "Fitting Experiment with Theory in Ar-OH"	23rd March 1990
Brimble Dr. M.A. (Massey University, New Zealand) "Synthetic Studies Towards the Antibiotic Griseusin-A"	29th July 1991

Brookhart Prof. M.S. (University of N. Carolina) — 20th June 1991
"Olefin Polymerizations, Oligomerizations and Dimerizations Using Electrophilic Late Transition Metal Catalysts"

Brown Dr. J. (Oxford University) — 28th February 1991
"Can Chemistry Provide Catalysts Superior to Enzymes?"

Bushby Dr. R. (Leeds University) — 6th February 1991
"Biradicals and Organic Magnets"

Butler Dr. A.R. (St. Andrews University) — 15th February 1989
"Cancer in Linxiam: The Chemical Dimension"

Butler Dr. A. (St. Andrews University) — 7th December 1989
"The Discovery of Penicillin: Facts and Fancies"

Cadogan Prof. J.I.G. (British Petroleum) — 10th November 1988
"From Pure Science to Profit"

Casey Dr. M. (University of Salford) — 20th April 1989
"Sulphoxides in Stereoselective Synthesis"

Cheetham Dr. A.K. (Oxford University) — 8th March 1990
"Chemistry of Zeolite Cages"

Clark Prof. D.T. (ICI Wilton) — 22nd February 1990
"Spatially Resolved Chemistry (using Nature's Paradigm in the Advanced Materials Arena)"

Cole-Hamilton Prof. D.J. (St. Andrews University) — 29th November 1989
"New Polymers from Homogenous Catalysis

Cowley Prof. A.H. (University of Texas) — 13th December 1990
"New Organometallic Routes to Electronic Materials"

Crich Dr. D. (University College London) — 27th April 1989
"Some Novel Uses of Free Radicals in Organic Synthesis"

Crombie Prof. L. (Nottingham University) — 15th February 1990
"The Chemistry of Cannabis and Khat"

Crout Prof. D.(Warwick University) — 29th November 1990
"Enzymes in Organic Synthesis"

Dingwall Dr. J. (Ciba-Geigy) "Phosphorus-containing Amino Acids: Biologically Active Natural and Unnatural Products"	18th October 1988
Dobson Dr. C.M. (Oxford University) "NMR Studies of Dynamics in Molecular Crystals"	6th March 1991
Dyer Dr. U. (Glaxo) "Synthesis and Conformation of C-Glycosides"	31st January 1990
Errington Dr.R.J. (University of Newcastle-upon-Tyne) "Polymetalate Assembly in Organic Solvents"	1st March 1989
Floriani Prof. C. (University of Lausanne,Switzerland) "Molecular Aggregates - A Bridge between Homogenous and Heterogenous Systems"	25th October 1989
Frey Dr. J. (Southampton University) "Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl"	11th May 1989
German Prof. L.S. (USSR Academy of Sciences - Moscow) "New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes"	9th July 1990
Gerrard Dr. D. (British Petroleum) Raman Spectroscopy for Industrial Analysis"	7th November 1990
Graduate Chemists (Polytechnics and Universities in North East England) "R.S.C. Symposium for presentation of papers by postgraduate students"	12th April 1989
Graham Dr D. (B.P. Research Centre) "How Proteins Adsorb to Interfaces"	4th December 1989
Greenwood Prof. N.N. (University of Leeds) Novel Cluster Geometries in Metalloborane Chemistry	9th November 1989
Hall Prof. L.D. (Addenbrooke's Hospital, Cambridge) "NMR - A Window to the Human Body"	2nd February 1989
Hardgrove Dr. G.(St. Olaf College, U.S.A.) "Polymers in the Physical Chemistry Laboratory"	December 1988

Harwood Dr. L.(Oxford University) — 25th January 1988
"Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions: Chemistry under Pressure"

Holloway Prof. J.H. (University of Leicester) — 1st February 1990
"Noble Gas Chemistry"

Hudlicky Prof. T. (Virginia Polytechnic Institute) — 25th April 1991
"Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products"

Hughes Dr. M.N. (Kings College, London) — 30th November 1989
"A Bug's Eye View of the Periodic Table"

Huisgen Prof. R. (Universitat Munchen) — 15th December 1989
"Recent Mechanistic Studies of (2+2) Additions"

Jackson Dr. R. (Newcastle University) — 31st October 1990
"New Synthetic Methods: alpha-Amino Acids and Small Rings"

Jager Dr. C. (Friedrich-Schiller University GDR) — 9th December 1988
"NMR Investigations of Fast Ion Conductors of the NASICON Type"

Jennings Prof. R.R. (Warwick University)
"Chemistry of the Masses" — 26th January 1989

Johnson Dr.B.F.G. (Cambridge University) — 23rd February 1989
"The Binary Carbonyls"

Klinowski Dr. J. (Cambridge University) — 13th December 1989
"Solid State NMR Studies of Zeolite Catalysts"

Kocovsky Dr. P. (Uppsala University) — 6th November 1990
"Stereo-Controlled Reactions Mediated by Transition and Non-Transition Metals"

Lacey Dr. D. (Hull University) — 31st January 1991
"Liquid Crystals"

Lancaster Rev. R. (Kimbolton Fireworks) — 8th February 1990
"Fireworks - Principles and Practice"

Logan Dr. N. (Nottingham University) — 1st November 1990
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